UNIVERSITY OF MAINE
LIBRARY

Class no. ~~S 48.6~~

Book no. ~~L846~~

Accession no. 83,213

LIBRARY
UNIV OF MAINE

LIBRARY
UNIV OF MAINE

ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY.

LIBRARY
UNIV. OF MAINE

LIBRARY
UNIV OF MAINE

ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY

FOR 1926.

ISSUED BY THE CHEMICAL SOCIETY.

Committee of Publication:

Chairman: N. V. Sidgwick, M.A., Sc.D., F.R.S.

H. B. Baker, C.B.E., D.Sc., F.R.S.
E. C. C. Baly, C.B.E., F.R.S.
H. Bassett, D.Sc., Ph.D.
H. V. A. Briscoe, D.Sc.
F. G. Donnan, C.B.E., M.A., F.R.S.
H. W. Dudley, O.B.E., M.Sc., Ph.D.
U. R. Evans, M.A.
J. J. Fox, O.B.E., D.Sc.
C. S. Gibson, O.B.E., M.A.
R. W. Gray, O.B.E., Ph.D.
A. J. Greenaway, F.I.C.
T. A. Henry, D.Sc.
C. K. Ingold, D.Sc., F.R.S.
H. King, D.Sc.
H. McCombie, D.S.O., M.C., D.Sc.
W. H. Mills, Sc.D., F.R.S.
T. S. Moore, M.A., B.Sc.
G. T. Morgan, O.B.E., D.Sc., F.R.S.
K. J. P. Orton, M.A., F.R.S.
J. R. Partington, M.B.E., D.Sc.
J. C. Philip, O.B.E., D.Sc., F.R.S.
R. H. Pickard, D.Sc., F.R.S.
T. S. Price, O.B.E., D.Sc., F.R.S.
F. L. Pyman, D.Sc., F.R.S.
R. Robinson, D.Sc., F.R.S.
J. F. Thorpe, C.B.E., D.Sc., F.R.S.

Editor:
Clarence Smith, D.Sc.

Assistant Editor:
A. D. Mitchell, D.Sc.

Indexer:
Margaret Le Pla, B.Sc.

Contributors:

F. W. Aston, M.A., D.Sc., F.R.S.
S. Barratt, B.A.
W. L. Bragg, F.R.S.
H. V. A. Briscoe, D.Sc.
J. A. V. Butler, M.Sc.
J. E. Coates, O.B.E., D.Sc.
J. C. Drummond, D.Sc.
B. A. Ellis, M.A.
J. J. Fox, O.B.E., D.Sc.
W. N. Haworth, D.Sc., Ph.D.
T. A. Henry, D.Sc.
C. K. Ingold, D.Sc., F.R.S.
H. J. Page, M.B.E., B.Sc.

Vol. XXIII.

LONDON:
GURNEY & JACKSON, 33 PATERNOSTER ROW, E.C.4.
1927.

PRINTED IN GREAT BRITAIN BY
RICHARD CLAY & SONS, LIMITED,
BUNGAY, SUFFOLK.

LIBRARY
UNIV OF MAINE

CONTENTS.

PAGE

GENERAL AND PHYSICAL CHEMISTRY. By J. E. Coates, O.B.E., D.Sc., and J. A. V. Butler, M.Sc. 11

INORGANIC CHEMISTRY. By H. V. A. Briscoe, D.Sc. . . . 49

ORGANIC CHEMISTRY:—

Part I.—Aliphatic Division. By W. N. Haworth, D.Sc., Ph.D. . 74

Part II.—Homocyclic Division. By C. K. Ingold, D.Sc., F.R.S. . 112

Part III.—Heterocyclic Division. By T. A. Henry, D.Sc. . . 150

ANALYTICAL CHEMISTRY. By J. J. Fox, O.B.E., D.Sc., and B. A. Ellis, M.A. 186

BIOCHEMISTRY. By J. C. Drummond, D.Sc., and H. J. Page, M.B.E., B.Sc. 209

CRYSTALLOGRAPHY. By W. L. Bragg, F.R.S. 257

SUB-ATOMIC PHENOMENA AND RADIOACTIVITY. By F. W. Aston, M.A., D.Sc., F.R.S. 280

SPECTROSCOPY. By S. Barratt, B.A. 296

83, 213

TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

Abbreviated Title.	Journal.
A.	Abstracts in Journal of the Chemical Society.
A.	British Chemical Abstracts,* Section A.
Abhandl. Kennt. Kohle	Gesammelte Abhandlungen zur Kenntnis der Kohle.
Amer. Chem. J.	American Chemical Journal.
Amer. J. Physiol.	American Journal of Physiology.
Amer. J. Sci.	American Journal of Science.
Amer. Rev. Tuberculosis	American Review of Tuberculosis.
Anal. Fis. Quím.	Anales de la Sociedad Española Física y Química.
Analyst	The Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Appl. Biol.	Annals of Applied Biology.
Ann. Bot.	Annals of Botany.
Ann. Chim.	Annales de Chimie.
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
Ann. Chim. Appl.	Annali di Chimica Applicata.
Ann. Physik	Annalen der Physik.
Ann. Physique	Annales de Physique.
Ann. Reports	Annual Reports of the Chemical Society.
Ann. Rep. Appl. Chem.	Annual Reports on the Progress of Applied Chemistry.
Arch ital. Biol.	Archives italiennes de Biologie.
Arch. Pharm.	Archiv der Pharmazie.
Arch. Sci. phys. nat.	Archives des Sciences physiques et naturelles.
Arkiv Kem. Min. Geol.	Arkiv för Kemi, Mineralogi och Geologi.
Astrophys. J.	Astrophysical Journal.
Atti R. Accad. Lincei	Atti (Rendiconti, Memorie) della Reale Accademia Nazionale dei Lincei, classe di scienze fisiche, matematiche e naturali, Roma.
B.	British Chemical Abstracts,* Section B.
Bäkt. Abhandl.	Centralanstalten för försökoväsendet på jordbruksområdet Bakteriologiska avdelningen (German trnsl.).
Ber.	Berichte der Deutschen Chemischen Gesellschaft.
Ber. Deut. bot. Ges.	Berichte der Deutschen botanischen Gesellschaft.
Biochem. J.	The Biochemical Journal.
Biochem. Z.	Biochemische Zeitschrift.
Bot. Gaz.	Botanical Gazette.
Brennstoff Chem.	Brennstoff Chemie.
Bull. Acad. Sci. Roumaine	Bulletin de la Section Scientifique de l'Académie Roumaine.
Bull. int. Acad. Polonaise	Bulletin international de l'Académie Polonaise des Sciences.
Bull. Sci. Pharm.	Bulletin des Sciences Pharmacologiques.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Bull. Soc. chim. Belg.	Bulletin de la Société chimique de Belgique.

* The year is not inserted in references to 1926.

Abbreviated Title.	Journal.
Bull. Soc. Chim. biol.	Bulletin de la Société de Chimie biologique.
Carnegie Inst. Washington	Carnegie Institute of Washington Publications.
Cellulosechem.	Cellulosechemie.
Chem. and Ind.	Chemistry and Industry.
Chem. Listy	Chemické Listy pro Vědu a Průmysl. Organ de la "Ceská chemická Společnost pro Védu a Průmysl."
Chem. News	Chemical News.
Chem. Reviews	Chemical Reviews.
Chem. Weekblad	Chemisch Weekblad.
Chem. Ztg.	Chemiker Zeitung.
Chem. Zentr.	Chemisches Zentralblatt.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Compt. rend. Soc. Biol.	Comptes rendus hebdomadaires de Séances de la Société de Biologie.
Compt. rend. Trav. Lab. Carlsberg	Comptes rendus des Travaux du Laboratoire Carlsberg.
Cornell Univ. Agr. Expt. Sta. Memoir	Cornell University Agricultural Experiment Station Memoirs.
Deuts. Landw. Presse	Deutsche Landwirtschaftliche Presse.
Gas- u. Wasserfach	Gas- und Wasserfach.
Gazzetta	Gazzetta chimica italiana.
Giorn. Chim. Ind. Appl.	Giornale di Chimica Industriale ed Applicata.
Helv. Chim. Acta	Helvetica Chimica Acta.
Ind. Eng. Chem.	Industrial and Engineering Chemistry.
J.	Journal of the Chemical Society.
Jahresb.	Jahresbericht über die Fortschritte der Chemie.
J. Agric. Res.	Journal of Agricultural Research.
J. Agric. Sci.	Journal of Agricultural Science.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Amer. Med. Assoc.	Journal of the American Medical Association.
J. Amer. Pharm. Assoc.	Journal of the American Pharmaceutical Association.
J. Amer. Soc. Agron.	Journal of the American Society of Agronomy.
J. Amer. Water Works Assoc.	Journal of the American Water Works Association.
J. Bact.	Journal of Bacteriology.
J. Biochem (Japan)	Journal of Biochemistry (Japan).
J. Biol. Chem.	Journal of Biological Chemistry.
J. Canada Med. Assoc.	Journal of the Canadian Medical Association.
J. Chem. Education	Journal of Chemical Education.
J. Chim. phys.	Journal de Chimie physique.
J. Coll. Agric. Hokkaido Imp. Univ.	Journal of the College of Agriculture, Hokkaido Imperial University, Japan.
J. Dept. Agric. Kyushu Univ.	Journal of the Department of Agriculture, Kyushu University.
J. Exper. Med.	Journal of Experimental Medicine.
J. Franklin Inst.	Journal of the Franklin Institute.
J. Gen. Physiol.	Journal of General Physiology.
J. Indian Chem. Soc.	Quarterly Journal of the Indian Chemical Society.
J. Opt. Soc. Amer.	Journal of the Optical Society of America.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Physical Chem.	Journal of Physical Chemistry.
J. Physiol.	Journal of Physiology.
J. Physique.	Journal de Physique.
J. Phys. Radium	Journal de Physique et le Radium.
J. Pom. Hort. Sci.	Journal of Pomology and Horticultural Science.
J. pr. Chem.	Journal für praktische Chemie.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.

Abbreviated Title.	Journal.
J. Soc. Chem. Japan	Journal of the Chemical Society of Japan. (Nippon Kwagaku Kwai Shi.)
J. Soc. Dyers Col.	Journal of the Society of Dyers and Colourists.
J. Text. Inst.	Journal of the Textile Institute.
Klin. Woch.	Klinische Wochenschrift.
Koll. Chem. Beihefte	Kolloidchemische Beihefte.
Kolloid-Z.	Kolloid Zeitschrift.
Landw. Jahrb.	Landwirtschaftliche Jahrbücher.
Landw. Jahrb. Schweiz	Landwirtschaftliche Jahrbücher Schweize.
Landw. Versuchs-Stat.	Die Landwirtschaftlichen Versuchs-Stationen.
Medd. K. Vetenskapsakad. Nobel-Inst.	Meddelanden från Kunglig-Vetenskapsakademiens Nobel-Institut.
Mem. Coll. Sci. Kyoto	Memoirs of the College of Science, Kyoto Imperial University.
Mem. Manchester Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Mikrochem.	Mikrochemie.
Mitt. wiss. tech. Arb. Republ. (Russ.)	Mitteilungen über wissentschaflich-technischen Arbeit in der Republik (Russ.).
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Naturwiss	Die Naturwissenschaften.
New York Agric. Exp. Stat.	New York Agricultural Experiment Station Bulletins.
P.	Proceedings of the Chemical Society.
Pflüger's Archiv.	Archiv für die gesamte Physiologie des Menschen und der Thiere.
Pharm. Weekblad	Pharmaceutisch Weekblad.
Pharm. Zentr.	Pharmazeutische Zentralhalle.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Physical Rev.	Physical Review.
Physikal. Z.	Physikalische Zeitschrift.
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. Imp. Acad. Tokyo.	Proceedings of the Imperial Academy of Japan.
Proc. K. Akad. Wetensch. Amsterdam	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
Proc. Nat. Acad. Sci.	Proceedings of the National Academy of Sciences.
Proc. Physical Soc.	Proceedings of the Physical Society of London.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Soc. Exp. Biol. Med.	Proceedings of the Society for Experimental Biology and Medicine.
Rec. trav. chim.	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
Rocz. Chem.	Roczniki Chemji organ Polskiego Towarzystwa Chemicznego.
S. Afr. J. Sci.	South African Journal of Science.
Scientific Agric.	Scientific Agriculture.
Sci. Papers Inst. Phys. Chem. Res. Tokyo	Scientific Papers of the Institute of Physical and Chemical Research, Tokyo.
Sci. Proc. Roy. Dublin Soc.	Scientific Proceedings of the Royal Dublin Society.
Sci. Rep. Tôhoku Imp. Univ.	Science Reports, Tôhoku Imperial University.
Sitzungsber. Heidelberg. Akad. Wiss.	Sitzungsberichte der Heidelberger Akademie der Wissenschaften.
Sitzungsber. Preuss. Akad. Wiss. Berlin	Sitzungsberichte der Preussischen Akademie der Wissenschaften zu Berlin.
Soc. Scient. Fennicae	Acta Societatis Scientiarum Fennicae.
Soil Sci.	Soil Science.
Stahl u. Eisen	Stahl und Eisen.

Abbreviated Title.	Journal.
Svensk Kem. Tidskr. . .	Svensk Kemisk Tidskrift.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Faraday Soc. . .	Transactions of the Faraday Society.
Trans. Roy. Soc. Canada .	Transactions of the Royal Society of Canada.
Ukraine Chem. J. . .	Ukrainian Chemical Journal.
Verh. deut. physikal. Ges. .	Verhandlungen der deutschen physikalischen Gesellschaft.
Wiss. Veröff. Siemens-Konz.	Wissenschaftliche Veröffentlichungen aus dem Siemens-Konzern.
Z. anal. Chem. . . .	Zeitschrift für analytische Chemie.
Z. angew. Chem. . . .	Zeitschrift für angewandte Chemie.
Z. anorg. Chem. . . .	Zeitschrift für anorganische und allgemeine Chemie.
Z. Chem. Pharm. . .	Zeitschrift für Chemie und Pharmacie (Erlenmeyer und Lewinstein).
Z. deuts. Geol. Ges. . .	Zeitschrift der deutschen Geologischen Gesellschaft.
Z. Elektrochem. . . .	Zeitschrift für Elektrochemie.
Z. Krist.	Zeitschrift für Krystallographie.
Z. Pflanz. Dung. . .	Zeitschrift für Pflanzenernährung und Düngung.
Z. Physik	Zeitschrift für Physik.
Z. physikal. Chem. . .	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Z. physikal. chem. Unterr.	Zeitschrift für den physikalischen und chemischen Unterricht.
Z. physiol. Chem. . .	Hoppe-Seyler's Zeitschrift für physiologsiche Chemie.

ERRATUM.

Annual Reports for 1925.

Page	Line	
172	6*	*for* "tetra-acetyl" *read* "tetra-cetyl."

* From bottom.

ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY.

GENERAL AND PHYSICAL CHEMISTRY.

No attempt is made to report progress in more than a few fields. The output of work on solutions of electrolytes warrants a continuation of last year's Report on this subject, and a section on reaction velocity in such solutions is added. References to optical activity and mutarotation seem desirable as a sequel to the 1924 Report. Subjects not recently dealt with are entropy, chemical constants, and electrification at surfaces.

The Third Law of Thermodynamics and the Entropies of Solids and Liquids.

Perhaps the most fundamental of physico-chemical problems is the relation between the maximum work and the corresponding total energy change of a chemical reaction. A knowledge of this relation in general would enable all kinds of chemical equilibria to be calculated from thermal data alone (heats of reaction at suitable temperatures, and the heat capacities of substances from absolute zero up to the highest temperature for which the equilibrium is to be calculated). The relation may be stated most simply in terms of the entropy change in the reaction by means of the equation $\Delta A - \Delta U = -T \,.\, \Delta S$, or by the analogous equation $\Delta F - \Delta H = -T \,.\, \Delta S$. Here, ΔU is the total-energy increase in the reaction, $\Delta H = \Delta U + P \,.\, \Delta V$ the "heat content" increase (*i.e.*, the heat absorbed in a reaction at constant pressure), ΔA the maximum work done on the system, and $\Delta F = \Delta A + P \,.\, \Delta V$ the free-energy increase of the system. The problem therefore reduces to a consideration of the entropy changes in reactions.

The concept of entropy as a quantity which can be definitely evaluated is chiefly due to G. N. Lewis and G. E. Gibson, who made the first systematic tabulation of the entropies of elements and compounds.[1] The entropy of a solid at a temperature T, referred to its entropy at absolute zero, is given by the integral

[1] *J. Amer. Chem. Soc.*, 1917, **39**, 2554; *A.*, 1918, ii, 29.

$\Delta S_0^T = \int_0^T (C_p/T) \, . \, dT$, where C_p is its heat capacity; and the entropies of liquids and gases are obtained by summing similar expressions for all the heat changes required to bring them from the solid crystalline state at absolute zero to the given temperature.

The entropy change in a chemical reaction involves, in addition to the entropies of the substances concerned (referred to absolute zero), a knowledge of the entropy change in the reaction at absolute zero, since $\Delta S_T = \Delta S_0 + \Sigma \Delta S_0^T$. The third law of thermodynamics as formulated by Nernst was equivalent to the statement that the entropy change in all reactions of "condensed" systems (solids or liquids) is zero at the absolute zero of temperature. In 1920, Lewis and Gibson [2] showed that this could not be true when supercooled liquids or solid solutions are involved, and they proposed to restrict the law to crystalline bodies, stating it thus: "If the entropy of each element in the crystalline form be taken as zero at absolute zero, the entropy of any pure crystal at absolute zero is zero, and the entropy of any other substance is greater than zero." E. D. Eastman [3] has since argued that there is a complete series of gradations from a perfectly crystalline substance to the haphazard arrangement in an amorphous solid, and that complicated systems of a low order of symmetry may have appreciable positive entropy. L. Pauling and R. C. Tolman, however, deny this and, in a statistical investigation of the entropy of supercooled liquids,[4] conclude that the entropy of a perfect crystal at the absolute zero is not dependent on the complexity of the unit of crystal structure. The third law may be tested by comparing the entropy change in a reaction as deduced from equilibrium measurements $[\Delta S_T = (\Delta H - \Delta F)/T]$ with the entropy change $(\Sigma \Delta S_0^T)$, calculated from the heat capacities. Lewis and Gibson, in their 1917 paper, showed that the available data, of somewhat low accuracy, supported the law (in its more general form). In 1920, G. E. Gibson, W. M. Latimer, and G. S. Parks [5] found that the thermal entropies of formation of formic acid and urea were in good agreement with the values obtained from equilibrium measurements. In 1922, Lewis, Gibson, and Latimer [6] drew up a revised table of entropies and demonstrated, in a number of cases, close agreement with the requirements of the law. T. J. Webb [7] has obtained a further confirmation in the cases of hydrated

[2] *J. Amer. Chem. Soc.*, 1920, **42**, 1529; *A.*, 1920, ii, 585.
[3] *Ibid.*, 1924, **46**, 39; *A.*, 1924, ii, 143.
[4] *Ibid.*, 1925, **47**, 2148; *A.*, 1925, ii, 952.
[5] *Ibid.*, 1920, **42**, 1533; *A.*, 1920, ii, 585.
[6] *Ibid.*, 1922, **44**, 1008; *A.*, 1922, ii, 471.
[7] *J. Physical Chem.*, 1925, **29**, 816; *A.*, 1925, ii, 867.

cadmium chloride ($CdCl_2,2{\cdot}5H_2O$) and cadmium iodide. H. L. J. Bäckström [8] investigated the change aragonite ⟶ calcite for the same purpose, but found a difference, which he ascribed to an error in the specific-heat curve of calcite at low temperatures.

Further work has been done to confirm the conclusion that supercooled liquids and solutions have greater entropy than the corresponding pure crystals. The first test of the point by Gibson, Parks, and Latimer [9] with solutions of ethyl and propyl alcohol was inconclusive. R. Wietzel [10] found that there is probably an entropy difference between amorphous and crystalline forms of silica at absolute zero. G. E. Gibson and W. F. Giauque [11] showed that supercooled liquid glycerol almost certainly has a greater entropy than the crystalline form. Now F. Simon and F. Lange [12] have reinvestigated these cases and find in the case of silica an entropy difference of $0{\cdot}9 \pm 0{\cdot}3$ unit, and in the case of glycerol $4{\cdot}6 \pm 0{\cdot}3$ units, at absolute zero.

The third law, in the form given it by Lewis and Gibson, is being used to determine the free energies of substances which cannot be conveniently determined by equilibrium measurements. Thus G. S. Parks and K. K. Kelley [13] have determined the entropies of the oxides of magnesium, calcium, aluminium, and (ferric) iron and of magnetite at 25° by heat-capacity measurements and have obtained therefrom values of the free energies. Similar measurements have been made with zinc oxide.[14] The free energy so determined is in good agreement with the values obtained by direct methods, for which data are in this case available. The free energies of the following organic compounds have been determined by the same method: Methyl, ethyl, and *n*-butyl alcohols [15]; *iso*propyl alcohol, acetone, ethylene glycol, acetic acid, and palmitic acid [16]; *tert.*-butyl alcohol, mannitol, erythritol, and *n*-butyric acid [17]; *n*-propyl alcohol, ethyl ether, and dulcitol.[18]

The entropy of a solid substance could evidently be calculated from its complete specific-heat equation. Whilst the specific-heat equations for solids at low temperatures account well for the form

[8] *J. Amer. Chem. Soc.*, 1925, **47**, 2432; *A.*, 1925, ii, 1162.
[9] *Ibid.*, 1920, **42**, 1542; *A.*, 1920, ii, 586.
[10] *Z. anorg. Chem.*, 1921, **116**, 71; *A.*, 1921, ii, 504.
[11] *J. Amer. Chem. Soc.*, 1923, **45**, 93; *A.*, 1923, ii, 124.
[12] *Z. Physik*, 1926, **38**, 227; **A.**, 1000.
[13] *J. Physical Chem.*, 1926, **30**, 47; **A.**, 232.
[14] C. G. Maier, G. S. Parks, and C. T. Anderson, *J. Amer. Chem. Soc.*, 1926, **48**, 2564; **A.**, 1210.
[15] G. S. Parks, *ibid.*, 1925, **47**, 338; *A.*, 1925, ii, 491.
[16] G. S. Parks and K. K. Kelley, *ibid.*, p. 2089; *A.*, 1925, ii, 949.
[17] G. S. Parks and C. T. Anderson, *ibid.*, 1926, **48**, 1506; **A.**, 784.
[18] G. S. Parks and H. M. Huffman, *ibid.*, p. 2788.

of the curve, an exact calculation of entropy on the same basis is not yet feasible.

Attempts have been made to find empirical equations for the entropies of solids at a given temperature. According to Latimer,[19] the entropy of an atom in a solid is a function of its mass, M, and of the constraints by which it is held. At temperatures at which the specific heats have reached the equipartition value the constraints are held to be the same, and Latimer found that the entropies of 16 salts at 25° were given by the sum of terms, $S_{298°} = \frac{3}{2}R \log M - 0{\cdot}94$, for all the atoms in the salt. This equation does not apply to the metals themselves. E. D. Eastman [20] has attempted to introduce a term depending on the constraints of the atoms and has found that the equation

$$S_{298°} = \tfrac{3}{2}R \log M + R \log \beta^{3/2}/V + 42{\cdot}1,$$

where V is the atomic volume and β the compressibility, gives approximately the entropies of many metals. Recently R. M. Buffington and W. M. Latimer [21] have made some accurate measurements of the coefficients of expansion of solids at low temperatures. Their measurements confirm the relation of E. Grüneisen [22] that the ratio of the specific heat to the volume coefficient of expansion of a substance is nearly independent of the temperature. They use this ratio ($C_p/3\alpha$, where α is the linear coefficient of expansion) for expressing the "constraints" of different substances and find that the equation

$$S_{298°} = \tfrac{3}{2}R \log M + R \log V - \tfrac{3}{2}R \log (C_p/3\alpha)_{T=160°} + 26{\cdot}5$$

gives the experimental entropies of a number of metals. It also applies to salts when M is replaced by the geometrical mean of the weights of the ions.

The Entropies of Gases and Dissolved Substances.

Simple thermodynamical considerations lead to the following equation for the entropy S of a mol. of perfect monatomic gas, at temperature T and pressure p:

$$S = \tfrac{5}{2}R \log T - R \log p + S_0 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

O. Sackur [23] showed that the constant S_0 is proportional solely to $M^{3/2}$, where M is the molecular weight of the gas, and the equation becomes

$$S = \tfrac{5}{2}R \log T - R \log p + \tfrac{3}{2}R \log M + [S]_0 \quad . \quad . \quad . \quad (2)$$

[19] *J. Amer. Chem. Soc.*, 1921, **43**, 818; *A.*, 1921, ii, 380.
[20] *Ibid.*, 1923, **45**, 80; *A.*, 1923, ii, 124.
[21] *Ibid.*, 1926, **48**, 2305; **A.**, 1088.
[22] *Ann. Physik*, 1908, [iv], **26**, 211; *A.*, 1908, ii, 563.
[23] *Ibid.*, 1911, [iv], **36**, 958; *A.*, 1912, ii, 145.

where $[S]_0$ is a universal constant. H. Tetrode, and later Sackur,[24] evaluated this constant from statistical considerations, obtaining the expression

$$[S]_0 = R \log \{(2\pi)^{3/2} k^{5/2} \varepsilon^{5/2} / h^3\} \quad . \quad . \quad . \quad . \quad . \quad (2a)$$

where k is the gas constant per molecule ($= R/N$), ε is the electronic charge and h is Planck's quantum constant. G. N. Lewis [25] has also made a calculation of $[S]_0$ on the basis of his theory of "ultimate rational units." The expression obtained (in the same notation) is

$$[S]_0 = R \log \{k^{5/2} c^3 / N^{3/2} (4\pi\varepsilon)^6\}$$

where c is the velocity of light. The values of these expressions are $-2{\cdot}30$ (Tetrode) and $-2{\cdot}63$ (Lewis). Experimental values are not known with sufficient accuracy to permit a decision between the two expressions, but theoretical considerations appear to favour the Tetrode expression.[26]

R. C. Tolman [27] determined the entropies of a number of gases indirectly from vapour-pressure data and, except in a few cases in which a large extrapolation had to be made, found good agreement with (2). Lewis, Gibson, and Latimer [28] showed that in four cases for which direct thermal data were available (He, A, Cd, and Hg vapours), there was remarkable agreement between the theoretical and experimental values. It may be noted, however, that the data were not sufficiently accurate to distinguish between the two values of $[S]_0$ above. More recently, W. H. Rodebush and A. L. Dixon [29] have determined the entropies of vapours of zinc and lead by vapour-pressure measurements and find good agreement with the theoretical values. Similar measurements with sodium vapour by Rodebush and T. de Vries [30] show only moderate agreement. Tolman has also shown [31] that if an atmosphere of electrons be considered as a monatomic gas, its entropy, as nearly as it can be computed from various thermionic data, agrees with the theoretical value.

The molecules of polyatomic gases may possess rotational and vibrational energy which must be taken into account in calculating their entropies. Tolman [32] made the assumption that the entropy

[24] *Ann. Physik*, 1912, **38**, 434; 1913, **40**, 67; *A.*, 1913, ii, 128. O. Stern gave a kinetic deduction of the same equation, *Physikal. Z.*, 1913, **14**, 629.

[25] *Physical Rev.*, 1921, ii, **18**, 121.

[26] Compare H. C. Hicks and A. C. G. Mitchell, *J. Amer. Chem. Soc.*, 1926, **48**, 1520; **A.**, 784.

[27] *Ibid.*, 1920, **42**, 1185; *A.*, 1920, ii, 468. [28] *Loc. cit.*, ref. (6).

[29] *Ibid.*, 1925, **47**, 1036; *A.*, 1925, ii, 492.

[30] *Ibid.*, p. 2488; *A.*, 1925, ii, 1142.

[31] *Ibid.*, 1921, **43**, 1592; *A.*, 1922, ii, 18.

[3] *Ibid.*, 1920, **42**, 1185; *A.*, 1920, ii, 468. *Loc. cit.*, ref. (27).

of any gas is the sum of the entropy of a perfect monatomic gas under the same conditions and the entropies of its rotational and vibrational energies. These are given by $\int_0^T C_r.d \log T$, where $C_r = C_p - \frac{5}{2}R$ is the difference between the actual heat capacity of the gas and the value for a monatomic gas. Only in one case, that of hydrogen, of which the heat capacity drops to the value for a monatomic gas above its boiling point, can this equation be applied to experimental data. Good agreement was found in this case.

Attempts have been made to evaluate this integral by theoretical calculations of the rotational and vibrational energies. In the case of a diatomic gas, it appears that only rotational energy need be considered. H. C. Urey has attempted [33] to evaluate the rotational energy of such gases by the use of an expression of F. Reiche [34] which gives the rotational energy of a molecule in a state characterised by two quantum numbers n_1, n_2 as $\epsilon = h^2(n_1 + n_2^2)/8\pi I^2$, where I is the moment of inertia of the molecule. The relative numbers of molecules in different quantum states are given by statistical equations; I is obtained from the maxima λ_1, λ_2 of the band spectrum by the classical equation $I = kT[\lambda_1\lambda_2/\pi c(\lambda_2 - \lambda_1)]^2$. Similar methods are applied to symmetrical polyatomic gases, *e.g.*, methane. R. C. Tolman and R. M. Badger extended this method,[35] and recently H. C. Hicks and A. C. G. Mitchell [36] have made a careful study of hydrogen chloride from the same point of view. Using "half quantum" numbers to specify the possible rotational states of the molecule they find the value of $\int C_r.d \log T$ between 0° K. and 298° K. to be 6·75. The value of the total entropy obtained by adding this to the corresponding entropy for a monatomic gas agrees well with the experimental figure.

Another method of dealing with rotational energies is by the use of an equation [37] deduced by O. Sackur, H. Tetrode, and others:

$$S = \tfrac{5}{2}R \log T + \tfrac{3}{2}R \log M + R \log V + \Sigma\tfrac{1}{2}R \log I_{1,2,3} + S_2 \quad . \quad (3)$$

[33] *J. Amer. Chem. Soc.*, 1923, **45**, 1445; *A.*, 1923, ii, 533.

[34] *Ann. Physik*, 1919, [iv], **58**, 657.

[35] *J. Amer. Chem. Soc.*, 1923, **45**, 2277; *A.*, 1923, ii, 830. Compare R. C. Tolman, *Physical Rev.*, 1923, ii, **22**, 470.

[36] *J. Amer. Chem. Soc.*, 1926, **48**, 1520; **A.**, 784. *Loc. cit.*, ref. (26).

[37] O. Sackur, *Ann. Physik*, 1913, [iv], **40**, 87; *A.*, 1913, ii, 128; H. Tetrode, *ibid.*, 1912, [iv], **38**, 441; L. Schames, *Physikal. Z.*, 1920, **21**, 38; *A.*, 1920, ii, 172; R. C. Tolman, *J. Amer. Chem. Soc.*, 1921, **43**, 866; *A.*, 1921, ii, 381; P. Ehrenfest and V. Trkal, *Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 162; *A.*, 1920, ii, 738; *Ann. Physik*, 1921, **65**, 609.

where I_1, I_2, I_3 are the moments of inertia. This equation cannot be employed directly, owing to lack of information about moments of inertia. Urey expressed his results in terms of this equation, substituting the moments of inertia obtained by the method described above. Latimer and Eastman [38] have given various empirical equations for the entropies of diatomic gases.

A further important advance in this field has been made by W. M. Latimer and R. M. Buffington,[39] who have calculated for the first time the entropies of inorganic ions in aqueous solution. Knowing the entropies of the solid salts and the heat-content and free-energy changes on solution, it is possible to calculate their entropies in solution. The entropies are obtained for a "hypothetical molar concentration," *i.e.*, they are obtained from data at very small concentrations and converted to the corresponding values at unit (molar) concentration on the assumption that the solution remains ideal. Although expressed as entropies in a (hypothetical) molar solution, they refer therefore to the properties of ions at great dilutions.

It is only possible to obtain in this way the sum of the entropies of the ions of the salts; but relative values for individual ions, referred to the entropy of the hydrogen ion as zero, are readily obtained and are sufficient for most purposes. The authors further calculated the entropies of the ions in the gaseous state by the equation for perfect gases and thus obtained values for the entropies of solution of gaseous ions. The values so obtained exhibit a remarkable parallelism with the energies of solution of the gaseous ions.[40] Further, when these entropies were plotted against the atomic radii of the ions as deduced from the crystal measurements of W. H. and W. L. Bragg, a linear relationship was discovered for ions of each charge. It is concluded that the entropy of solution of gaseous ions is to a high degree a function solely of the size and charge of the ion.

The relative entropies of ions in aqueous solution can be applied to a great variety of thermodynamical problems. A number of examples are given in this paper, and in a further paper W. M. Latimer [41] has used the data to calculate the normal potential of the fluorine electrode.

[38] *Loc. cit.*, refs. (19) and (20).

[39] *J. Amer. Chem. Soc.*, 1926, **48**, 2297; **A.**, 1102. K. F. Herzfeld attempted to calculate electrolytic normal potentials on the assumption that the entropies of dissolved ions are the same as in the gaseous state at the same concentration (*Ann. Physik*, 1918, [iv], **56**, 133; *A.*, 1918, ii, 289). Later he reversed the calculation and estimated from normal potentials and solubilities, the "bound energy" ($= TS$) of ions relative to the silver ion (*Z. Elektrochem.*, 1922, **28**, 460; *A.*, 1923, ii, 12).

[40] W. M. Latimer, *ibid.*, 1926, **48**, 1234; **A.**, 648.

[41] *Ibid.*, p. 2868.

Chemical Constants.

The so-called "chemical constants," or integration constants of the Clausius vapour-pressure relation, $d \log p/dT = \Delta H/RT^2$, are intimately connected with the entropies of the corresponding gases. Since investigations in the two fields have been carried on by different groups of workers practically independently, it is convenient to deal with them separately, but the results in one field have obvious bearings on the other.

In the earlier attempts to evaluate chemical constants by Nernst and his school, empirical equations for the variations of heat capacities with temperature were employed which were wide of the truth at low temperatures.[42] The true integration constant is obtained by giving ΔH its value $\Delta H = \Delta H_0 + \int_0^T \Delta C_p \, . \, dT$, where ΔC_p is the difference between the heat capacities of gas and solid, whence

$$\log p = -\frac{\Delta H_0}{RT} + \int \frac{\int_0^T \Delta C_p \, . \, dT}{RT^2} \, . \, dT + i,$$

and accurate heat-capacity data at low temperatures are required to determine the integration constant i. For a perfect gas having constant heat capacity C_p down to absolute zero, $iR + C_p = S_0 - S_0^s$, where S_0 is the entropy constant of the gas [equation (1)] and S_0^s the entropy of the condensed phase at absolute zero. According to the Nernst heat theorem, S_0^s is zero [42a]; hence, for a monatomic gas, the Sackur–Tetrode calculation [referred to the above equation (2a)] leads to the value $i = \log \{(2\pi m)^{3/2} k^{3/2}/h^3\}$. Using gram-molecular weights and converting to common logarithms we obtain the chemical constant $C = C_0 + \frac{3}{2} \log_{10} M$, where C_0 is a universal constant numerically equal to $-1{\cdot}589$.

A. C. G. Egerton [43] collected the available experimental data for ten substances (based on measured vapour pressures except in two cases) and obtained a weighted mean $-1{\cdot}596 \pm 0{\cdot}008$, in good agreement with the theoretical value. F. Simon,[44] however, using values of C determined for 14 elements, found considerable deviations which appeared to increase with increasing heat of vaporisation. Notable divergences are exhibited by the elements sodium and potassium, as first observed by R. Ladenburg and R. Minkowski.[45] Recent investigations have confirmed these

[42] Compare A. C. G. Egerton, *Phil. Mag.*, 1920, [vi], **39**, 1; *A.*, 1920, ii, 84.

[42a] According to Lewis and Gibson this must be limited to crystalline solids, see ref. (2).

[43] *Proc. Physical Soc.*, 1925, **37**, 75; *A.*, 1925, ii, 277.

[44] *Z. physikal. Chem.*, 1924, **110**, 572; *A.*, 1925, ii, 98; *ibid.*, 1926, **123**, 404; **A.**, 1103. Compare K. Wöhl, *ibid.*, 1924, **110**, 166; *A.*, 1925, ii, 98.

[45] *Z. Physik*, 1921, **8**, 137; *A.*, 1922, ii, 191.

discrepancies. F. Simon and W. Zeidler [46] have redetermined the heat capacities of these elements at low temperatures and obtain values of C greater than the theoretical values by $+ 0{\cdot}52 \pm 0{\cdot}23$ (Na) and $+ 0{\cdot}33 \pm 0{\cdot}32$ (K). W. Edmondson and Egerton,[47] whilst criticising certain of these calculations, have substantially confirmed this result.

In the calculation of the Sackur–Tetrode expression, identical "quantum weight factors" are assigned to solid and vapour phases. If the identity of these factors is not assumed a more general expression is obtained, *viz.*, $i = \log \{g_g/g_s \,.\, (2\pi m)^{3/2}k^{3/2}/h^3\}$, where g_g and g_s are the weight factors for the gaseous and solid states. The nature of the quantum weight factors has been discussed by A. Einstein,[48] O. Stern,[49] W. Schottky,[50] and R. H. Fowler.[51] If $g_g/g_s = 2$, i will be greater than the Sackur–Tetrode value by $\log 2$. In the case of the alkali metals, according to Schottky there is spectroscopic evidence for $g_g = 2$, and if $g_s = 1$ the experimental values are approximately accounted for.

In the last equation, the term g_s refers to the solid (or condensed) phase. It implies a finite entropy of the condensed phase $S_0^s = R \log g_s$. A. Eucken and F. Fried [52] have attempted to determine whether solids have finite entropies at absolute zero by comparing the integration constants, i_k, of the equilibrium-constant equation of a number of gaseous reactions, with Σi, the algebraic sum of the vapour-pressure constants of the substances concerned. These two quantities are only identical if all values of S_0^s are zero. They find differences outside the experimental error in most cases. These would be covered by a zero entropy of $\pm R \log 2$, but the data are not sufficiently precise for a quantitative agreement to be made out. Fried [53] has made a further test of the same point by determining electromotively the free energy of reactions of the type $MO + H_2 = M + H_2O$ (M = Hg, Pb, or 2Ag), and comparing it with calculated values involving the chemical constant of hydrogen. It is claimed that the results indicate finite zero-entropies. It may be observed that it is not entirely clear that these calculations are always referred to the solids as condensed phases.

Little progress has been made in accounting for the chemical

[46] *Z. physikal. Chem.*, 1926, **123**, 383; **A.**, 1103.
[47] *Proc. Roy. Soc.*, 1927, [*A*], **113**, 520, 533.
[48] *Verh. deut. physikal. Ges.*, 1914, **16**, 820.
[49] *Ann. Physik*, 1916, [iv], **49**, 823; *A.*, 1916, ii, 379.
[50] *Physikal. Z.*, 1921, **22**, 1; *A.*, 1921, ii, 179; *ibid.*, 1922, **23**, 9, 448.
[51] *Phil. Mag.*, 1923, [vi], **44**, 1, 497; 1926, [vii], **1**, 845; **A.**, 553.
[52] *Z. Physik*, 1924, **29**, 36; *A.*, 1925, ii, 97.
[53] *Z. physikal. Chem.*, 1926, **123**, 406; **A.**, 1105.

constants of polyatomic molecules. The following equation for that part of the chemical constant which is dependent on rotational energy, $i_r = \log (8\pi^2 \bar{I} k/h^2\sigma)$, where $\bar{I}$ is the geometrical mean of the moments of inertia of the molecule and σ a symmetry factor, has been obtained in a number of ways [54] [compare equation (3)]. A. Eucken, E. Karwat, and F. Fried [55] determined the chemical constants of a number of gases and compared them with the value obtained by adding the above term to the " monatomic " constant, using optical values of $\bar{I}$ and ignoring the factor σ. The results showed no concordance, which might be ascribed to the absence of the factor σ. Mention may be made of recent determinations of chemical constants of the following: Chlorine,[56] bromine,[57] iodine,[58] and hydrogen halides.[59] No satisfactory agreement has been obtained between the values (between which large discrepancies often occur) and the theory.

In the Sackur–Tetrode calculation, the quantum theory is implicitly applied to the translational motions of gases, whilst in calculations of chemical constants it is assumed that that part of the heat capacity which depends on the translational energy is a constant down to the absolute zero. W. Nernst [60] employed a degradation theory according to which the heat capacities of gases fell off at low temperatures in the same way as do those of solids, and obtained a value $i = \log \{(2\pi m)^{3/2} k^{5/2}/\varepsilon h^3\}$, which is almost indistinguishable numerically from the Sackur–Tetrode value. The conditions which must be fulfilled by a gas the heat capacity of which falls off to zero at absolute zero have been examined by K. Bennewitz,[61] whilst the difficult question of the applicability of quantum theory to the translational motions in gases has been discussed by several authors.[62] F. I. G. Rawlins [63] has recently

[54] Ref. (37). Also M. Saha and R. Sur, *Phil. Mag.*, 1926, [vii], **1**, 279; **A.**, 234; K. Széll, *Z. Physik*, 1926, **36**, 292; **A.**, 570.

[55] *Z. Physik*, 1924, **29**, 1; *A.*, 1925, ii, 98; also A. Eucken and E. Karwat, *Z. physikal. Chem.*, 1924, **112**, 467; *A.*, 1924, ii, 820.

[56] R. R. S. Cox, *Proc. Camb. Phil. Soc.*, 1925, **22**, 491; *A.*, 1925, ii, 645.

[57] R. Suhrmann and K. von Lüde, *Z. Physik*, 1924, **29**, 71; *A.*, 1925, ii, 96; K. Jellinek, *Z. anorg. Chem.*, 1926, **152**, 16; **A.**, 569.

[58] K. Jellinek and R. Uloth, *ibid.*, **151**, 157; **A.**, 463.

[59] F. I. G. Rawlins, *Trans. Faraday Soc.*, 1926, **22**, 233; **A.**, 1087.

[60] Z. *Elektrochem.*, 1916, **22**, 185; *A.*, 1916, ii, 469.

[61] *Z. physikal. Chem.*, 1924, **110**, 725; *A.*, 1925, ii, 97.

[62] A. Einstein, *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1924, 261; 1925, 3, 18; *A.*, 1925, ii, 495, 624; M. Planck, *ibid.*, 1925, 49; *A.*, 1925, ii, 495; A. Schidlof, *Arch. Sci. phys. nat.*, 1924, [v], **6**, 281, 381; *A.*, 1925, ii, 483; *ibid.*, 1926, [v], **8**, 5; **A.**, 463; E. Schrödinger, *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1925, 434; *A.*, 1925, ii, 951; *Physikal. Z.*, 1926, **27**, 95; **A.**, 463.

[63] *Proc. Physical Soc.*, 1926, **38**, 176; **A.**, 567.

summarised some aspects of the present state of knowledge of specific heats at low temperatures and chemical constants.

Solutions of Electrolytes.

Rapid progress continues in this field. In continuation of the 1925 Report,[1] the following investigations for the purpose of further testing the Debye–Hückel theory of strong electrolytes may be noted. The limiting law for tervalent ions has been confirmed by solubility measurements of $[Co(NH_3)_6]^{\cdots}[Co(CN)_6]'''$ in sodium chloride solutions.[2] The effect of the dielectric constant of the medium has been confirmed by measurements of the activity coefficients of hydrogen chloride in aqueous glycerol solutions,[3] and by similar measurements in sucrose solutions.[4] The effect of temperature as predicted by the theory has been confirmed [5] by solubility measurements of silver iodate at 75°. The theory has been tested in certain non-aqueous solvents. Thus T. J. Webb [6] has studied the freezing-point depressions of some salts in acetic acid and in liquid ammonia, obtaining results which are mainly in agreement with the theory. Similar measurements with *cyclo*hexanol as solvent show good agreement with the equations.[7]

In his extension of the theory to concentrated solutions, it will be remembered that E. Hückel attempted to take into account the effect of varying dielectric constant of the solutions, and, on the assumption that the dielectric constant varies linearly with the ion concentrations (*i.e.*, $D = D_0 - \Sigma\delta c$), he found that the corresponding term in the expression for $\log f$ was approximately proportional to the concentration.[8] G. Scatchard [9] has tested this equation for aqueous and alcoholic solutions of hydrogen chloride, and finds that it is in good agreement with the data up to $1M$. H. S. Harned [10] has studied the activity coefficients of hydrogen chloride in concentrated chloride solutions with the same object, and finds that there is "remarkable agreement between the observed results and the general theory of Debye and Hückel. In fact, nothing

[1] *Ann. Report*, 1925, **22**, 27.

[2] J. N. Brönsted and N. J. Brumbaugh, *J. Amer. Chem. Soc.*, 1926, **48**, 2015; **A.**, 907.

[3] W. W. Lucasse, *Z. physikal. Chem.*, 1926, **121**, 254; **A.**, 796; *J. Amer. Chem. Soc.*, 1926, **48**, 626; **A.**, 474.

[4] G. Scatchard, *ibid.*, p. 2026; **A.**, 911.

[5] W. P. Baxter, *ibid.*, p. 615; **A.**, 474.

[6] *Ibid.*, p. 2263; **A.**, 1102.

[7] E. Schreiner and O. E. Frivold, *Z. physikal. Chem.*, 1926, **124**, 1; **A.**, 1208.

[8] *Ann. Report*, 1925, **22**, 34, equation (6).

[9] *J. Amer. Chem. Soc.*, 1925, **47**, 2098; *A.*, 1925, ii, 971.

[10] *Ibid.*, 1926, **48**, 326; **A.**, 354.

seriously contradictory to their general theory has developed from the numerous results on chloride solutions considered." It is found that in solutions of constant total ionic strength $\log f_{HCl}$ is proportional to its concentration up to $3M$. Values of δ for the salts are obtained from the Hückel expression, and making the arbitrary assumption that $\delta_{K^\cdot} = \delta_{Cl'}$, relative values are obtained for the ions. In the case of lithium and hydrogen chlorides, these values are so great as to lead to negative values of the dielectric constant in solutions above $4M$. It is suggested that the linear variation of $\log f$ with concentration (when interionic electrical effects according to the simpler theory have already been taken into account) has a deeper significance than Hückel's theory implies. G. Åkerlöf has made a similar study of sulphate solutions.[11] The value of δ for the sulphate ion is negative, *i.e.*, it is more polarisable than water and increases the dielectric constant of the medium. All the available data of single and mixed salt solutions are collected in a paper by H. S. Harned and G. Åkerlöf.[12] Good agreement with the Hückel expression is exhibited in solutions of single electrolytes, but only moderate agreement in mixed electrolytes. Åkerlöf [13] has further put forward the idea that the solubility of a salt is higher the greater its effect (positive or negative) on the dielectric constant of the medium. Using the values of δ obtained above, he shows that there is a close parallelism between the two quantities.

The linear variation of $\log f$ with concentration has also been confirmed by E. Güntelberg [14] for hydrochloric acid in (HCl, MCl) mixtures of constant total-ion concentration. This is shown to be a consequence of J. N. Brönsted's rule [15] of the linear variation of the osmotic coefficient in such solutions, and to apply only to mixtures of salts of the same ion-type. The same author has discussed Brönsted's principle of the specific interaction of ions [15] and its relation to the Debye–Hückel theory. According to this principle, the activity coefficient of an ion is made up of two factors : (1) a coefficient of interaction between the ion and other ions present, and (2) a " salting-out " coefficient depending solely on the other ions present. In factor (1), it is supposed that ions are uniformly influenced by ions of their own sign and that specific effects arise only from the interaction of ions of opposite sign. The physical basis of this principle is found in the Debye–Hückel

[11] *J. Amer. Chem. Soc.*, 1926, **48**, 1160; **A.**, 688.
[12] *Physikal. Z.*, 1926, **27**, 411; **A.**, 796.
[13] *J. Physical Chem.*, 1926, **30**, 1585.
[14] *Z. physikal. Chem.*, 1926, **123**, 199; **A.**, 1207.
[15] *J. Amer. Chem. Soc.*, 1922, **44**, 877; *A.*, 1922, ii, 481; *ibid.*, 1923, **45**, 2898; *A.*, 1924, ii, 94.

conception, according to which there is in the immediate vicinity of any one ion, a great preponderance of ions of the opposite sign and these only are responsible for the specific effects. The Debye–Hückel theory appears to be superior in that it obtains directly the interionic electrical effects of all kinds. Brönsted's formulation is, however, advantageous in the interpretation of relations in certain types of mixed salt solutions (*e.g.*, solubilities of slightly soluble salts in solutions of various ion-types).

In the last Report, it was pointed out that there is a difference between the Milner and the Debye and Hückel calculations of the interionic electrical energy (the former being two-thirds of the latter). This difference has now been elucidated. E. Q. Adams [16] has pointed out that the quantity obtained by Debye and Hückel in their first calculation is the free energy change (ΔF) due to interionic electrical forces, in the *transfer* of ions from a given solution to a very dilute solution in which electrical forces are negligible. Debye and Hückel directly evaluated, in fact, the electrical work done in removing an ion from its ion atmosphere. Milner, on the other hand, calculated the electrical work done in separating the ions of a given solution to an infinite distance from one another. This is the maximum (electrical) work done in an infinite dilution (A; Adams's ΔA). Since the latter is two-thirds of the former, the discrepancy is explained.

Debye and Hückel regarded the quantity obtained by them as the mutual potential energy of the ions in solution (U_e) and attempted to determine the corresponding work term by means of the Gibbs–Helmholtz equation $A/T = -\int U_e/T^2 \,.\, dT$. In order to get a result of the correct form, they were obliged to treat the dielectric constant as independent of the temperature. Since U_e is itself a free-energy quantity, it is necessary to reverse this process to get the true total-energy change. In this way, E. Q. Adams and N. Bjerrum [17] find that the heat of dilution of a salt solution is given by $\Delta U = -\frac{3}{2}A(1 + d \log D/d \log T)$. N. Bjerrum approaches the matter on the basis of Debye's second calculation, in which he obtained the electrical work of charging all the ions in the solution (reversibly) simultaneously. This corresponds to A, the electrical work of dilution. Debye calculated the corresponding free energies of transfer of ions by obtaining the differential of A for a small addition of one ion species:

$$\delta A/\delta n_i = A_i = -\epsilon^2 \kappa z_i^2/2D.$$

Bjerrum greatly simplified the derivation by showing that the

[16] *J. Amer. Chem. Soc.*, 1926, **48**, 621; **A.**, 474.
[17] *Z. physikal. Chem.*, 1926, **119**, 145; **A.**, 476.

same result may be obtained by considering the electrical work of charging a single ion in the given solution. J. A. V. Butler [18] has shown by an independent argument that the quantity so obtained is in reality a free-energy quantity.

There appears to be considerable uncertainty about the value of $d \log D/d \log T$ above; Adams gives $-1{\cdot}5$, Bjerrum $-1{\cdot}315$. Apart from this, Bjerrum compared recorded heats of dilution of salt solutions with this equation. The experimental figures (necessarily referring to moderately concentrated solutions) are highly specific and show little relation to the calculated value. W. Nernst and W. Orthmann [19] have determined the heats of dilution of some salts at very low concentrations. They find even among salts of the same ion-type no agreement with the equation; in fact, some give positive and others negative values. The theory of the heat effects corresponding to the free-energy changes is therefore unsatisfactory.

The claim of G. Nonhebel and H. Hartley [20] that Milner's theory accounts better than Debye's for the activity coefficients of hydrogen chloride in methyl alcohol is disputed by G. Scatchard.[21] The former authors, however, question [22] his method of dealing with the data. G. Nonhebel [23] has investigated the activity coefficients of hydrochloric acid at extreme dilutions. He finds that the equation $\log_{10} f = -0{\cdot}39\sqrt{c}$ best fits the results; the Debye–Hückel theory gives $\log_{10} f = -0{\cdot}505\sqrt{c}$, whilst Milner's gives approximately $\log_{10} f = -0{\cdot}37\sqrt{c}$.

The problem of the determination of the activity coefficients of an individual ion-species in a salt solution has received some attention. If the activity coefficients of one kind of ion (*e.g.*, chlorine ion) of a salt were known, it would be possible, by correlating the salts, to determine them in all cases. D. A. MacInnes [24] attempted this method by making the assumption that the two ions of potassium chloride (which have nearly the same weight and mobility) have the same activity coefficients at each concentration. G. N. Lewis and M. Randall adopted the same assumption.[25]

The individual activity coefficients could be measured directly in a concentration cell " with transport " if the value of the liquid-junction potential were known, since the *E.M.F.* of such a cell

[18] *Phil. Mag.*, 1927, [vii], **3**, 213.
[19] *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1926, 51; **A.**, 579.
[20] *Ann. Report*, 1925, **22**, 33.
[21] *Phil. Mag.*, 1926, [vii], **2**, 577; **A.**, 1006.
[22] *Ibid.*, p. 586; **A.**, 1006. [23] *Ibid.*, p. 1085.
[24] *J. Amer. Chem. Soc.*, 1919, **41**, 1086; *A.*, 1919, ii, 385; *ibid.*, 1921, **43**, 1217; *A.*, 1921, ii, 619.
[25] " Thermodynamics," 1923, p. 381.

(*e.g.*, $H_2|HClc_1|HClc_2|H_2$) is given by $RT/F \cdot \log a_1/a_2 + E_L$, where E_L is the liquid-junction potential. H. S. Harned [26] has subjected the "thermodynamic method" of computing liquid-junction potentials, first used by D. A. MacInnes and J. A. Beattie,[27] to a rigorous analysis and has obtained data for the individual ion activities in mixed chloride solutions.

According to the theory of electrolytic dissociation as formulated by Arrhenius, the degree of dissociation of an electrolyte is given by $\alpha = \Lambda_c/\Lambda_\infty$. In the case of strong electrolytes, a decisive mass of evidence indicates that dissociation is complete at all dilutions, and variations in the equivalent conductivity Λ_c must be ascribed to changes in the ionic mobilities with concentration. The dissociation of weak electrolytes, formerly calculated by the same formula, must now be corrected for variations in the ionic mobilities. M. S. Sherrill and A. A. Noyes [28] have considered several cases of "moderately ionised" acids. The true degree of dissociation is given, not by Λ_c/Λ_∞ but by Λ_c/Λ_e, where Λ_e is the value of the equivalent conductivity for complete dissociation at the particular concentration measured. Values of Λ_e are obtained by the Kohlrausch rule from the equivalent conductivities of completely ionised substances at the same concentrations, thus :

$$(\Lambda_e)_{c\,HA} = \Lambda_{c\,HCl} + \Lambda_{c\,NaA} - \Lambda_{c\,NaCl}.$$

The ionisation constants obtained from the true degrees of dissociation are further corrected for the effect of electrical forces by multiplying each ionic concentration by its activity coefficient, thus : $K_{HA} = (f_{H^\cdot}\alpha)(f_{A^\cdot}\alpha)/(1 - \alpha)c$. In this way, satisfactory constants are obtained for the first stage of ionisation of phosphoric and sulphurous acids, and for the second stage of ionisation of sulphuric acid, assuming in the last case that the first hydrogen is completely ionised. D. A. MacInnes [29] has applied similar methods to a number of weak acids and obtains excellent constants, except in the case of acetic acid, in which the values show a definite trend with concentration. This may be due to inaccurate data, or, it is suggested, to the effect of variations in the dielectric constant of the solution, which are not taken into account.

The variation of the ionic concentration of water in salt solutions has been studied. The true equilibrium constant of the ionisation of water is the activity constant

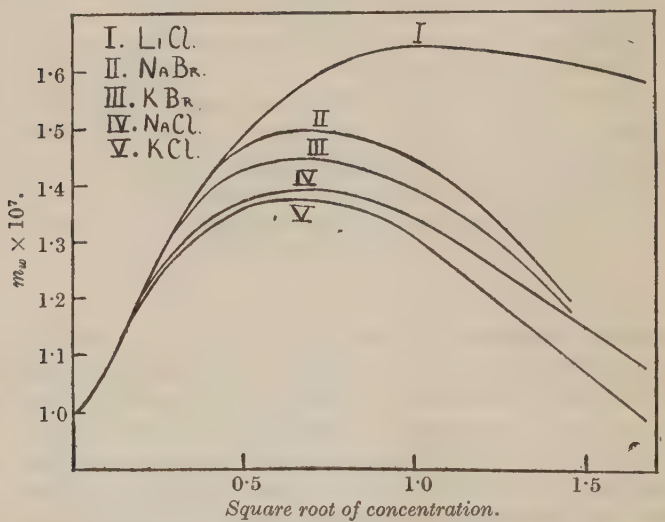
$$K_w = a_{H^\cdot} \cdot a_{OH^\cdot}/a_{H_2O} = f_{H^\cdot} \cdot f_{OH^\cdot} \cdot m_w^2/a_{H_2O},$$

where m_w is the concentration of hydrogen and hydroxyl ions in

[26] *J. Physical Chem.*, 1926, **30**, 433.
[27] *J. Amer. Chem. Soc.*, 1920, **42**, 1117; *A.*, 1920, ii, 466.
[28] *Ibid.*, 1926, **48**, 1861; **A.**, 1006. [29] *Ibid.*, p. 2068; **A.**, 906.

the solution. An increase of the dissociation of water and other weak electrolytes on the addition of salts was predicted by J. N. Brönsted.[30] Since the activity coefficients of ions initially decrease with increasing total-ion concentration, the concentrations m_w must increase in order to maintain the equilibrium constant. E. Schreiner[31] made some exact calculations of the effect on the basis of equations representing the effect of salt concentration on activity coefficients. The older electromotive methods of determining the ionic product of water involved cells with liquid junctions. A new method of determining relative values of the "activity coefficient product," $f_{H^\cdot} \cdot f_{OH'}/a_{H_2O}$, from a combination of data

FIG. 1.



from cells without liquid junctions, has been developed.[32] When this quantity is known, the ionic concentrations can be determined, since $m_w = m_{H^\cdot} = m_{OH'} = \sqrt{K_w/(f_{H^\cdot} \cdot f_{OH'}/a_{H_2O})}$. The dissociation of water in solutions of potassium and sodium chlorides,[32] bromides,[33] and sulphates[34] and of lithium chloride[35] has been determined in this way. The curves for the alkali-halide solutions are given in Fig. 1. The dissociation rises to a maximum at about

[30] *J. Amer. Chem. Soc.*, 1920, **42**, 761; *J.*, 1921, **119**, 574.
[31] *Z. anorg. Chem.*, 1924, **135**, 357; *A.*, 1924, ii, 524.
[32] H. S. Harned, *J. Amer. Chem. Soc.*, 1925, **47**, 930; *A.*, 1925, ii, 538.
[33] H. S. Harned and G. M. James, *J. Physical Chem.*, 1926, **30**, 1060; **A.**, 907.
[34] G. Åkerlöf, *loc. cit.*, Ref. (11).
[35] H. S. Harned and F. E. Swindells, *J. Amer. Chem. Soc.*, 1926, **48**, 126; **A.**, 245.

0·5*N*. In the sulphate solutions, the maximum value is greater and the curve flatter.

J. Colvin [36] has determined the ion-activity product of water in aqueous glycerol solutions, up to 40% glycerol, by means of electromotive measurements involving liquid junctions. He finds that the dissociation constant of water remains practically unchanged over the whole range.

Ion Hydration in Aqueous Solution.

A number of determinations of the degree of hydration of ions in aqueous solutions, by means of distribution experiments, have appeared. The principle of the method, first employed by J. C. Philip,[37] is that if the ions are combined with water, the amount of "free water" available for dissolving another substance is reduced. The distribution of a suitable substance between a non-aqueous solvent and the salt solution is studied. Assuming that the true distribution coefficient between the solvent and the "free water" is the same as in pure water, the amount of "free water" can be determined, and hence the amount combined with the ions. J. N. Sugden [38] has made an extensive series of measurements of the distribution of acetic acid between amyl alcohol and salt solutions, and has deduced the corresponding hydration figures. Except in the case of sulphates, the hydration values so obtained are practically independent of the concentration and, further, are additive for the ions of salts. Nitrates and chlorates were found to have *negative* hydration values, *i.e.*, they increase the apparent amount of water. Relations between the hydration figures and the viscosity and also the molecular conductivity at infinite dilution were found. For these reference must be made to the paper. Similar measurements have been made by S. Glasstone and collaborators,[39] who have determined the solubilities of ethyl acetate in salt and other solutions, and by H. A. Taylor,[40] who determined the partition ratio of hydrogen chloride between benzene and salt solutions. The latter concluded that there is no appreciable difference between "free" and combined water, the aqueous solutions behaving like pure water.

It should be observed that the validity of this method depends

[36] *J.*, 1925, **127**, 2788; **A.**, 245.

[37] *Trans. Faraday Soc.*, 1907, **3**, 140; *A.*, 1907, ii, 935; *J.*, 1907, **91**, 711.

[38] *J.*, 1926, 174; **A.**, 244.

[39] S. Glasstone and A. Pound, *ibid.*, 1925, **127**, 2660; **A.**, 1926, 18; S. Glasstone, D. W. Dimond, and E. C. Jones, *ibid.*, 1926, 2935; S. Glasstone, D. W. Dimond, and E. R. Harris, *ibid.*, p. 2939.

[40] *J. Physical Chem.*, 1925, **29**, 995; *A.*, 1925, ii, 858. Compare J. W. Corran and W. C. McC. Lewis, *J. Amer. Chem. Soc.*, 1922, **44**, 1673; *A.*, 1922, ii, 691.

entirely on the truth of the assumption that the solubility in the "free" water of a salt solution is the same as in pure water. The measurements give primarily the relative activity coefficients of the solute employed in various salt solutions, and the relations found are not necessarily to be interpreted as the result of hydration. The problem is identical with that of the "salting-out" effect of electrolytes on non-electrolytes, which has recently received much attention.

In many cases, in dilute solutions at any rate, the effect of an electrolyte on the solubility of a non-electrolyte is given by V. Rothmund's equation,[41] $\log s_0/s = kc$, where s_0 is the solubility in water, and s that in a salt solution of concentration c. J. S. Carter [42] has found that the solubility of iodine in salt solutions can in most cases be represented by this equation. K. Linderström-Lang [43] has made an extensive series of determinations of k for hydroquinone, quinone, boric acid, and succinic acid. A general explanation of the effect has not been found. A. McKeown found,[44] using P. C. L. Thorne's data,[45] that there was a correlation between the effect of sodium chloride on the solubility of ether in aqueous solutions and its effect on the heat of solution, a relation which has a statistical basis. Linderström-Lang finds that this is not general.

According to P. Debye and J. McAulay [46] the effect is due to the influence of the electric field of ions on other components of a solution, which causes the more polarisable molecules to amass themselves round the ion, and the less polarisable molecules to be displaced from the vicinity of ions. McAulay [47] has considered the effect of non-electrolytes on the solubilities of salts from the same point of view. He deduces a relation between the dielectric constant of the solvent and solubility, which accounts fairly well for the solubilities of salts in alcohol–water mixtures. He further outlines a theory suggested by Debye, of which greater detail is promised later, in which the distribution of water and alcohol molecules is given as a function of the distance from an ion. The curves show that the proportion of molecules of water (the more polarisable constituent) to alcohol increases rapidly at 1—2 Å.U. from the ion.

A new approach from which, it appears, conclusive evidence

[41] *Z. physikal. Chem.*, 1900, **33**, 401; *A.*, 1900, ii, 467; *ibid.*, 1909, **69**, 523; *A.*, 1909, ii, 980; also Setschenov, *ibid.*, 1889, **4**, 117; *A.*, 1889, 1044.
[42] *J.*, 1925, **127**, 2861; **A.**, 236.
[43] *Compt. rend. Trav. Lab. Carlsberg*, 1924, **15**, 1; *A.*, 1925, ii, 30.
[44] *J. Amer. Chem. Soc.*, 1922, **44**, 1203; *A.*, 1922, ii, 552.
[45] *J.*, 1921, **119**, 262.
[46] *Ann. Report*, 1925, **22**, 35.
[47] *J. Physical Chem.*, 1926, **30**, 1202; **A.**, 1089.

as to the nature of the hydration of ions may be obtained, has been opened up by the study of the energy changes in the solution of gaseous ions. These may be determined from certain atomistic data.[48] W. M. Latimer [49] has made some new calculations of the energy of solution of gaseous ions in water, making use of his ionic entropies, and finds a remarkable agreement between his values and those calculated by the expression of M. Born,[50] $\Delta E = (e^2/2r)(1 - 1/D)$, where r is the radius of an ion of charge e, and D is the dielectric constant of the solvent, using the ionic radii calculated by W. H. and W. L. Bragg from crystal measurements. This equation is a simple electrostatic expression for the energy change in bringing a charged sphere into a medium of dielectric constant D. Latimer's relation, already described,[51] that the entropies of solution of gaseous ions of one sign vary linearly with the same radii, again shows that the energy effects on the solution of gaseous ions are determined by their size and charge. In very dilute solutions, there is no evidence of specific ion–water combinations, though in concentrated solution specific effects depending on the nature of the ion may come in.

T. J. Webb has attempted a direct calculation of the free energies of solution of gaseous ions.[52] This quantity is regarded as being made up of two parts: (1) the difference between the energy required to charge the ion in the solution and in a vacuum; and (2) the work done in compressing the solvent owing to the effect of an electric field on the solvent "dipoles." The free energy of hydration is obtained as a function of the radius of the "cavity" containing the ion in the solution. This radius is obtained by use of the partial volumes of salts in solution. The apparent volume of a salt in solution is equal to the volumes of the ion cavities, less the contraction caused in the solution (electrostriction). An expression is deduced for the last quantity and by a combination of the equations it is possible to determine the radii of the ion cavities and the free energies of hydration. The values are checked by determining some corresponding lattice-energies of solid salts and electron affinities of halogens. It may be also observed that K. Jabłczyński [53] determined limiting volumes of salts in solution and found values in agreement with the crystal measurements of Bragg.

[48] *Ann. Report*, 1920, **17**, 3. Compare A. Gyemant, *Z. Physik*, 1924, **30**, 240.

[49] *J. Amer. Chem. Soc.*, 1926, **48**, 1234; **A.**, 684.

[50] *Z. Physik*, 1920, **1**, 45. [51] This Report, p. 17.

[52] *Proc. Nat. Acad. Sci.*, 1926, **12**, 524; **A.**, 1008; *J. Amer. Chem. Soc.*, 1926, **48**, 2589; **A.**, 1208.

[53] *Rocz. Chem.*, 1923, **3**, 362; *A.*, 1925, ii, 33.

Velocity of Reaction in Solutions.

As indicated in previous Reports,[1] research in this field, including the study of ion catalysis and salt action, has been much concerned with the significance of thermodynamic activity as a factor determining reaction velocity. Although this question is still open, there appears to be a fairly general conviction that activity is an important factor. The bearing of the modern theory of electrolytes is beginning to be explored.

J. N. Brönsted[2] has attempted a general formulation of the factors governing the rate of ionic reactions in dilute solutions, especially the kinetic salt effect, which is, broadly speaking, much greater in reactions between ions than between neutral molecules or neutral molecules and ions. Thermodynamical considerations, supplemented by the hypothesis that the rate of a reaction A + B = C + D is determined by the rate of formation of an unstable intermediate complex A,B (" critical complex "), lead to an expression for the velocity, $v = k \,.\, C_A C_B \,.\, f_A f_B / f_{A,B}$ (f is the activity coefficient), provided that a change of the medium (as, *e.g.*, in change of ion concentration) involves only activity, not concentration, change of the substrate. The charge of A,B is the algebraic sum of that of A and B. Taking the activity coefficients of ions to be determined only by their charges and the total ion concentration, and assuming A,B to behave as an ordinary ion, the sign and approximate magnitude of the activity factor $F = f_{z_A} f_{z_B} / f_{(z_A + z_B)}$ can be evaluated from activity data or from the approximate relation[3] $\log f = -z^2\sqrt{\mu}$, where z is the charge of the ion and μ the ionic strength, whence $v = kC_AC_Be^{2z_Az_B\sqrt{\mu}}$ approximately. For a reaction between a neutral molecule and an ion, F evidently represents the salt effect on the activity of the former, which, in dilute solution, is relatively small and approximately linear. For reactions between ions, considerable (exponential) salt effects are indicated—positive if the reacting ions have the same, negative if different signs. Experimental data agree with the theory, but not always quantitatively.[4] The influence of ions increases rapidly with their valency. In accordance with Brönsted's " principle of the specific interaction of ions,"[5] the activity coefficient of a

[1] *Ann. Report*, 1922, **19**, 18; 1924, **21**, 24; H. S. Taylor, " Physical Chemistry," p. 779.

[2] *Z. physikal. Chem.*, 1922, **102**, 169; *A.*, 1922, ii, 699; *ibid.*, 1925, **115**, 337; *A.*, 1925, ii, 681.

[3] J. N. Brönsted and V. K. La Mer, *J. Amer. Chem. Soc.*, 1924, **46**, 555; *A.*, 1924, ii, 306.

[4] A large number of examples are given by J. N. Brönsted, *loc. cit.*, ref. (2).

[5] See this Report, p. 22.

reactant ion is chiefly influenced by ions of the opposite sign, especially if multivalent.

Although recognising its practical value, N. Bjerrum [6] and J. A. Christiansen [7] criticise the theoretical basis of Brönsted's formula, which, however, the former deduces by assuming a different mechanism of reaction, and also from the kinetic theory. Christiansen obtains an expression in formal agreement with Brönsted's by applying the kinetic equation for a gas reaction to solutions,[8] account being taken of the increased "inactivation factor," and especially of the effect of interionic forces in modifying collision frequency and concentration near an ion. The nature and difficulties of the problem are further exemplified in relation to a study of the reaction between hydrogen peroxide and iodine ions,[9] in which the salt effect—slightly positive for the salt type KCl, slightly negative for the type K_2SO_4, positive and greater for the type $BaCl_2$—is attributed to changes in the proportion of hydrogen peroxide to water molecules around an iodine ion following the influence on its electric field of the surrounding cations. Factors such as the relative volumes, polarisability, and dipole properties of these molecules may be operative.[10]

G. Scatchard [11] has given a very general kinetic interpretation of activity by which he claims to justify the expression of reaction rates in terms of activities when rates are defined as "moles transformed in 1 mole of all components." With this modification, he is in agreement with the Brönsted expression.

Brief reference may be made to recent studies of reactions between ions :

(1) *Ions of the Same Sign* (Strong positive salt effect).—(*a*) Termolecular reduction of ferric chloride by stannous chloride : [12] bivalent have twice the effect of univalent cations, and the reaction is bimolecular at high salt concentration. (*b*) Bimolecular reaction between the cations of mercuric nitrate and chloropentamminocobaltic nitrate : [13] anions are much more effective than cations.

[6] *Z. physikal. Chem.*, 1924, **108**, 82; *A.*, 1924, ii, 240; *ibid.*, 1925, **118**, 251; **A.**, 131.

[7] *Ibid.*, 1924, **113**, 35; *A.*, 1925, ii, 47.

[8] Previously considered by M. Trautz, *Z. anorg. Chem.*, 1919, **106**, 149; *A.*, 1919, ii, 327.

[9] J. A. Christiansen, *Z. physikal. Chem.*, 1925, **117**, 433; **A.**, 1926, 33.

[10] See in this connexion *Ann. Report*, 1925, **22**, 35; this Report, p. 28.

[11] *J. Amer. Chem. Soc.*, 1923, **45**, 1581; *A.*, 1923, ii, 626.

[12] W. F. Timoféev, G. E. Muchin, and W. G. Gurevitsch, *Z. physikal. Chem.*, 1925, **115**, 161; *A.*, 1925, ii, 586.

[13] J. N. Brönsted and C. E. Teeter, *J. Physical Chem.*, 1924, **28**, 579; *A.*, 1924, ii, 745.

(*c*) Oxidation of iodide by ferricyanide.[14] (*d*) Saponification of esters of dibasic acids : [15] the first stage shows a small (linear) salt effect, the second a large positive (exponential) effect—the cationic charge is the chief factor and the activity factor F calculated from the ionic strength accounts for the observed rates. (*e*) The photodecomposition of uranyl formate in formic acid : [16] the magnitudes of salt effects are in good accord with Brönsted's theory.

(2) *Ions of Opposite Sign* (Strong negative salt effect).—(*a*) Reaction between hydrogen, iodine, and iodate ions; here the salt effect is quantitatively accounted for by the factor $F = 10^{-2\cdot20\sqrt{2\mu}}$ over a considerable range of ion concentration. The factor 2·20 is greater than the value calculated from the Debye theory. The reaction in acetate buffers is accounted for in a similar way.[17] (*b*) Reduction of ferric salts by thiosulphate.[18]

When the reacting system contains a weak electrolyte the addition of neutral salt may displace its equilibrium,[19] and the consequent change of concentration gives rise to a "secondary salt effect," the "primary effect" being due to activity change only.[20] The former depends on salt effects on the activity factor in the expression for the dissociation constant of the weak electrolyte :

$$K = ([A_{z_1}][B_{z_2}]/[(AB)_{z_3}])(f_{z_1}f_{z_2}/f_{z_3});$$

such activity effects can be calculated approximately on the basis of the interionic-attraction theory. The salt action is positive or negative according to the type of weak electrolyte. Writing the equilibrium as $A + B \rightleftharpoons C +$ catalyst ion, the general rule is : As the sum of the squares of the ionic charges of the reactants is greater or less than this sum for the resultants, so the secondary salt effect is negative or positive. This principle has been experimentally verified.[20] The catalytic decomposition of nitrosotriacetonamine by hydroxyl ions shows, *e.g.*, a positive effect in the presence of piperidine, negative in the presence of phosphate, and very little effect, as expected, in the presence of sodium aminoacetate [21] ($NH_2{\cdot}CH_2{\cdot}COO' + H_2O \rightleftharpoons NH_2{\cdot}CH_2{\cdot}CO_2H + OH'$).

[14] C. Wagner, *Z. physikal. Chem.*, 1924, **113**, 261; *A.*, 1925, ii, 49.

[15] J. N. Brönsted and A. Delbanco, *Z. anorg. Chem.*, 1925, **144**, 248; *A.*, 1925, ii, 684.

[16] G. Berger, *Rec. trav. chim.*, 1925, **44**, 47; *A.*, 1925, ii, 313.

[17] E. Abel and F. Stadler, *Z. physikal. Chem.*, 1926, **122**, 49; **A.**, 1009.

[18] J. Holluta and A. Martini, *Z. anorg. Chem.*, 1924, **140**, 206; **141**, 23; 1925, **144**, 321; *A.*, 1925, ii, 305, 215, 702.

[19] J. N. Brönsted, *J.*, 1921, **119**, 574.

[20] Ref. (13); J. N. Brönsted and C. V. King, *J. Amer. Chem. Soc.*, 1925, **47**, 2 523; *A.*, 1925, ii, 1171; J. N. Brönsted and K. Pedersen, *Z. physikal. Chem.*, 1924, **108**, 185; *A.*, 1924, ii, 331.

[21] M. Kilpatrick, *J. Amer. Chem. Soc.*, 1926, **48**, 2091; **A.**, 919.

(3) *Ions and Neutral Molecules.*—It is in the large class of reactions between neutral molecules and ions, including ion catalysis, that the question of the significance of activity has received the most attention. The unimolecular decomposition of hydrogen peroxide [22] in bromine–bromide solutions (virtually, catalysis by hydrogen bromide of constant concentration) is given by the equation

$$-d[H_2O_2]/dt = k_a[H_2O_2][H^\cdot][Br'] \cdot f^2_{HBr}$$

for ionic strengths not exceeding 1·0; the "concentration" velocity coefficient k_c (in contrast with the "activity" velocity coefficient, k_a) shows a marked drift. Similar relations apply to the chlorine–chloride reaction.[22] J. A. Christiansen [23] has criticised this formulation in the particular case of the above reaction. The conversion of *N*-chloroacetanilide into *p*-chloroacetanilide [24] is exactly proportional to the activity product of the hydrogen chloride catalyst. The rate of addition of hydrogen chloride to quinone in ethyl-alcoholic solution is stated [25] to be governed by the activity product of the hydrogen and chlorine ions. Proportionality between rate and activity is also supported in studies of the reaction between formic acid and bromine or iodine.[26]

S. W. Pennycuick [27] has attempted to settle the disputed question whether the inversion of sucrose follows strictly the unimolecular law. His very accurate measurements [28] show a small increase of k during reaction. Postulating that water molecules are activated by association with hydrogen ions, $v = k$ [sugar mols. per mol. H_2O][$H^\cdot$,nH_2O], the last term being assumed proportional to the hydrogen-ion activity which does apparently increase slightly during inversion. Previous investigators [29] found no evidence of the latter, but T. W. J. Taylor and R. F. Bomford [30] observed a 7% increase in the presence of salt. G. Scatchard's [31] analysis

[22] W. C. Bray and/or R. S. Livingston, *ibid.*, 1923, **45**, 1251; *A.*, 1923, ii, 473; *ibid.*, p. 2048; *A.*, 1923, ii, 747; *ibid.*, 1925, **47**, 2069; *A.*, 1925, ii, 981; *ibid.*, 1926, **48**, 45, 53, 405; **A.**, 245, 251, 364.

[23] *Z. physikal. Chem.*, 1925, **117**, 448; **A.**, 1926, 33.

[24] H. S. Harned and H. Seltz, *J. Amer. Chem. Soc.*, 1922, **44**, 1475; *A.*, 1922, ii, 631; A. C. D. Rivett, *Z. physikal. Chem.*, 1913, **82**, 201; **85**, 113; *A.*, 1913, ii, 202, 1041; G. Åkerlöf, *Medd. K. Vetenskapsakad. Nobel-Inst.*, 1922, **6**, No. 2.

[25] L. Ebert, *Z. Elektrochem.*, 1925, **31**, 113, 209; *A.*, 1925, ii, 408, 556.

[26] D. L. Hammick, W. K. Hutchison, and F. R. Snell, *J.*, 1925, **127**, 2715; **A.**, 1926, 32. D. L. Hammick and M. Zvegintzov, *J.*, 1926, 1105; **A.**, 691.

[27] *J. Amer. Chem. Soc.*, 1926, **48**, 6; **A.**, 249.

[28] *Ann. Report*, 1924, **21**, 14.

[29] H. A. Fales and J. C. Morrell, *J. Amer. Chem. Soc.*, 1922, **44**, 2071; *A.*, 1922, ii, 832; C. M. Jones and W. C. McC. Lewis, *J.*, 1920, **117**, 1120.

[30] *J.*, 1924, **125**, 2016; *A.*, 1924, i, 1286.

[31] *J. Amer. Chem. Soc.*, 1926, **48**, 2259; **A.**, 1107.

of Pennycuick's data indicates, however, constancy of rate to within a few parts per 1000, the observed increase being attributed to a systematic error. Scatchard [32] has come to the conclusion that the difficulties attending the accurate electrometric measurement of hydrogen-ion activity in sucrose solutions are such as to render inconclusive the previous attempts of himself [33] and others [34] to determine the mechanism of the inversion process by fitting the rates of reaction with formulæ containing this activity. It may here be noted that the same author, discussing the correlation of reaction rate and viscosity, indicates the great experimental difficulties involved, and shows that the kinetic theory requires no viscosity effect. A viscosity correction has been employed by W. C. McC. Lewis and others.[35]

The acid catalysis of lactone formation, which shows all the characteristic features of hydrolytic reactions, has been studied in water, ether, and water–ether mixtures by H. S. Taylor and H. W. Close.[36] New evidence is found for believing that the rate is determined by the hydrogen-ion activity only, the activity, viscosity, and hydration factors employed by previous investigators [37] being regarded as very uncertain.

According to M. Kilpatrick [38] the rate of decomposition of nitrosotriacetonamine by alkali is decreased in the presence of glycerol to about the same relative extent as the decrease of the hydroxyl-ion activity in J. Colvin's [39] measurements of hydrogen- and hydroxyl-ion activities in glycerol–water mixtures; the increased activity of the hydrogen-ion in such mixtures would explain the accelerating effect of glycerol in hydrogen-ion catalysis.

The theories of salt action mentioned above refer in the first place to dilute solutions. G. Grube and G. Schmid [40] find that the salt effect on the hydrolysis of cyanamide by dilute nitric acid in solutions of nitrates (linear at low salt concentrations) is exponential for concentrations from $1N$ to saturation; $k = k_0 e^{rc}$ where k and k_0 are velocity coefficients for solutions of the same

[32] *J. Amer. Chem. Soc.*, 1926, **48**, 2026; **A.**, 911.

[33] *Idem, ibid.*, 1923, **45**, 1581; *A.*, 1923, ii, 626; *ibid.*, 1921, **43**, 2387; *A.*, 1922, i, 230.

[34] T. Moran and W. C. McC. Lewis, *J.*, 1922, **121**, 1613; C. M. Jones and W. C. McC. Lewis, ref. (29).

[35] Ref. (29), and *Ann. Report*, 1922, **19**, 19; W. H. Garrett and W. C. McC. Lewis, *J. Amer. Chem. Soc.*, 1923, **45**, 1091; *A.*, 1923, ii, 476; J. Colvin, *Trans. Faraday Soc.*, 1926, **22**, 241; **A.**, 1109.

[36] *J. Physical Chem.*, 1925, **29**, 1085; *A.*, 1925, ii, 1070.

[37] Garrett and Lewis, ref. (35).

[38] Ref. (21).

[39] This Report, p. 27, ref. (36).

[40] *Z. physikal. Chem.*, 1926, **119**, 19; **A.**, 474; also G. Schmid and R. Olsen, *ibid.*, **124**, 97.

acidity containing respectively c and 0 equivalents of salt, and r is the "specific salt effect." This relation is valid for other reactions, whilst a similar relation, $a = a_0 e^{r'c}$, applies to the salt effect on the thermodynamic activities [41] except at low concentrations ($< 1N$) where, owing to interionic forces, a lowering of ion activity occurs. This law is considered incompatible with the "dual theory" of catalysis. The fact that r and r' are independent of temperature [42] does not agree with Bjerrum's theory that catalysis is determined by the equilibrium $H^{\cdot},nH_2O \rightleftharpoons H^{\cdot} + nH_2O$. Whilst Grube and Schmid's relation is in agreement with Hückel's activity expression,[43] Schmid and Olsen [42] prefer to account for deviations from the exponential law (activities) at low concentrations, not by the interionic-attraction theory, but on the basis of G. Tammann's theory of internal pressure.[44] From the measured external-pressure effect on the hydrogen-electrode potential (in the absence of free hydrogen gas),[45] and assuming internal-pressure changes due to the salt to exert the same effect on the electrode as external pressure, the true salt effect (total effect less pressure effect) on the hydrogen-ion activity is in agreement with the exponential equation at low as well as at high salt concentrations.

G. Åkerlöf,[46] in a very recent paper, gives strong evidence in favour of the general rule that the velocity always follows the activity of the catalyst ion for hydroxyl- as well as hydrogen-ion catalysis in salt solutions. In the hydroxyl-ion catalysis of the decomposition of diacetone alcohol the curves expressing the change, with salt concentration, of the reaction velocity and of the hydroxyl-ion activity are, for a series of chlorides, in the same order, just as in the acid catalysis of the N-chloroacetanilide transformation.[47] The salt effect on the hydroxyl-ion activity, thermodynamic and catalytic, is the reverse of that on the hydrogen-ion activity, and an attempt is made to relate reaction velocities in acid and alkaline salt solutions to the water equilibrium.[48] Åkerlöf [49] has found the relation $k/k_0 = (a/a_0)^{D/C^{2/3}}$ for the N-chloroacetanilide transformation in acid–salt solutions (D is a constant; C concentration of salt; and a, a_0 the hydrogen-ion activities

[41] For a review of the literature see ref. (40). See also this Report, p. 21.

[42] G. Schmid and R. Olsen, ref. (40), where further references and a discussion of Bjerrum's theory are given.

[43] *Ann. Report*, 1925, **22**, 34, equation (6); this Report, p. 21.

[44] G. Tammann, "Uber die Beziehungen zwischen den inneren Kräften und Eigenschaften der Lösungen" (Hamburg and Leipzig, 1907).

[45] G. Tammann and H. Diekmann, *Z. anorg. Chem.*, 1926, **150**, 129; **A.**, 360.

[46] *J. Amer. Chem. Soc.*, 1926, **48**, 3046.

[47] Refs. (24) and (46).

[48] This Report, p. 25.

[49] *Medd. K. Vetenskapsakad. Nobel-Inst.*, 1925, **6**, No. 2, 1; **A.**, 1926, 125.

with and without salt, respectively). His earlier relation [50] $k = c\sqrt[3]{a}$ for ester hydrolysis has been questioned.[51]

Following A. Lapworth,[52] N. Bjerrum [53] and others, F. O. Rice and associates [54] advocate a theory of unhydrated-ion catalysis ("protions," present in small concentration), which they extend to a general theory [55] that the velocity is determined by the concentration of "residual" molecules in equilibrium with other components of the system. The theory is largely based on a comparison of the temperature coefficients of similar reactions. The affinity for water of the hydrogen ion being greater than that of the hydroxyl ion, neutral solutions are "catalytically alkaline," and the catalytic minimum point for reactions catalysed by both ions should be at practically the same acidity for all such reactions. This minimum is in fact often found [56] at about p_H 5. Inconsistencies with the theory are indicated in that the minimum (p_H 4·8) for the autocatalytic reaction between iodine and acetone in aqueous solution is not affected by temperature and neutral salts,[56] and that the p_H values for benzamide and acetamide hydrolysis are higher than predicted, *viz.*, 5·8 and 6·2, respectively.[57]

Further support has been given to the theory [58] that substances subject to hydrolytic reaction in the presence of both acid and alkali (*e.g.*, esters) are weak ampholytes, the rate being determined by the concentration of the positive or negative ester ion, which is increased respectively by the acid or alkaline catalyst, and is calculable from the two equilibrium constants K_a and K_b. Assuming equal reactivity of these ions, the relation between rate and p_H

[50] *Ann. Report*, 1922, **19**, 19.

[51] Grube and Schmid, ref. (40); also ref. (46).

[52] *J.*, 1908, **93**, 2187; also J. Kendall and P. M. Gross, *J. Amer. Chem. Soc.*, 1921, **43**, 1416; *A.*, 1922, ii, 32.

[53] *Z. anorg. Chem.*, 1920, **109**, 275; also E. Schreiner, *ibid.*, 1922, **121**, 321; *A.*, 1922, ii, 468; *ibid.*, 1924, **135**, 333; *A.*, 1924, ii, 524.

[54] F. O. Rice and M. Kilpatrick, *J. Amer. Chem. Soc.*, 1923, **45**, 1401; *A.*, 1923, ii, 548; F. O. Rice and W. Lemkin, *ibid.*, p. 1896; *A.*, 1923, ii, 678; F. O. Rice, *ibid.*, p. 2808; *A.*, 1924, ii, 98; F. O. Rice, C. F. Fryling, and W. A. Wesolowski, *ibid.*, 1924, **46**, 2405; *A.*, 1925, ii, 48; F. O. Rice and C. F. Fryling, *ibid.*, 1925, **47**, 379; *A.*, 1925, ii, 556.

[55] The *general* character of this theory has been disputed; see C. N. Hinshelwood, *Chem. Reviews*, 1926, **3**, 230; *idem*, "The Kinetics of Chemical Change in Gaseous Systems," 1926, p. 155; R. C. Tolman, *J. Amer. Chem. Soc.*, 1925, **47**, 1525.

[56] For collected data see M. Bergstein and M. Kilpatrick, *J. Physical Chem.*, 1926, **30**, 1616.

[57] I. Bolin, *Z. anorg. Chem.*, 1925, **143**, 201; *A.*, 1925, ii, 411.

[58] H. von Euler and O. Svanberg, *Z. physiol. Chem.*, 1921, **115**, 139; *A.*, 1922, i, 219; H. von Euler and E. Rudberg, *Z. anorg. Chem.*, 1923, **127**, 244; *A.*, 1923, ii, 840; *Z. Physik*, 1923, **16**, 54; *A.*, 1923, ii, 547.

is given by a symmetrical U-curve with a minimum at the isoelectric point :

$$v = k_0 + k_{\text{cat.}}[\text{E}^{\cdot}] + k_{\text{an.}}[\text{E}'] = k_0 + k_{\text{cat.}}K_b[\text{H}^{\cdot}]/k_w + k_{\text{an.}}K_a/[\text{H}^{\cdot}]$$
$$= k_0 + B[\text{H}^{\cdot}] + A/[\text{H}^{\cdot}] \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where $\text{E}^{\cdot}$ and E′ are the ester ions and A and B are constants. Recent work [59] is in good agreement with the theory. Contrary to earlier observations,[60] the two limbs of the curve are of equal slope. Ethyl benzenesulphonate (non-ampholyte) shows quite different behaviour. Some doubt attaches to the significance of k_0; possibly it gives the activity of the " zwitterions." Salts have very little effect on the catalytic-minimum p_{H}. The inversion of sucrose has been discussed from the same point of view.[61]

Studies on the catalytic minimum of the iodine–acetone reaction (referred to above), in buffer solutions, have been made by H. M. Dawson and associates.[62] Not only is support found for the " dual " theory of catalysis, which has found little favour in recent years, but it is extended to the anion, the observed rates being given by the equation $v = k_{\text{H}\cdot}[\text{H}^{\cdot}] + k_{\text{HA}}[\text{HA}] + k_{\text{A}'}[\text{A}']$ with the addition of the term $k_{\text{OH}'}[\text{OH}']$ at low hydrogen-ion concentration. Assuming complete dissociation of the salt, and also the validity of the " concentration " expression for the dissociation constant, K_c, of the weak acid, a symmetrical U-curve is theoretically predicted when v is plotted against p_{H}, in excellent agreement with experimental data. Catalytic activity is proportional to volume concentration of the catalyst calculated from K_c, and no connexion is found between velocity and thermodynamic activity.

Mutarotation.

Recent research on the mechanism of mutarotation of the sugars is of interest in relation to the claim of J. W. Baker, C. K. Ingold, and J. F. Thorpe [63] to have obtained conclusive proof that this phenomenon is purely a tautomeric change involving (contrary to the previously accepted view) no intervention of water. According to T. M. Lowry and E. M. Richards,[64] the experimental results

[59] K. G. Karlsson, *Z. anorg. Chem.*, 1925, **145**, 1; *A.*, 1925, ii, 877.

[60] *Ibid.*, 1921, **119**, 69; *A.*, 1922, ii, 40; *Ann. Report*, 1922, **19**, 19.

[61] H. von Euler and A. Ölander, *Z. anorg. Chem.*, 1926, **156**, 143; **A.**, 1108.

[62] H. M. Dawson and J. S. Carter, *J.*, 1926, 2282; **A.**, 1108; H. M. Dawson and N. C. Dean, *ibid.*, p. 2872; H. M. Dawson and C. R. Hoskins, *ibid.*, p. 3166.

[63] *Ann. Report*, 1924, **21**, 13; *J.*, 1924, **125**, 268; *A.*, 1924, i, 262. These authors based their conclusions on a mathematical analysis of the dynamics of mutarotation, and on the observation that very small amounts of water had no effect on the velocity of mutarotation of tetra-acetyl glucose dissolved in ethyl acetate, and of glucose in methyl alcohol.

[64] *J.*, 1925, **127**, 1385; *A.*, 1925, i, 886; see also T. M. Lowry, *ibid.*, p. 1371; *A.*, 1925, i, 886 (a reply to Baker, Ingold, and Thorpe, and a general discussion of the mechanism of mutarotation).

of these authors were largely invalidated by the presence of unknown catalytically-active impurities, in the absence of which mutarotation can generally be suspended in a dry solution. Further, in the presence of the very small amounts of water used by Baker, Ingold, and Thorpe, the value of $dk/d[H_2O]$ should be so small as to be experimentally indistinguishable from the zero value which they found and regarded as incompatible with the "hydrate theory."

Lowry [64] has re-examined the whole question, and, on the basis of modern views on valency, has extended his mechanism for acid and alkaline ester-hydrolysis to the analogous mutarotation of the sugars, thus going far towards a reconciliation of previously conflicting views. Both phenomena are regarded as ionic in character. The former proceeds through the formation of bi-polar molecules (zwitterions) by addition of H^+ and OH^-, one of these being derived from the acid or alkali, the other from water, thus :

$$CH_3{\cdot}CO{\cdot}O{\cdot}CH_3 \rightleftharpoons CH_3{\cdot}\overset{\overset{\bar{O}}{\|}}{\underset{\underset{OH}{|}}{C}}{-}\overset{+}{O}{\cdot}CH_3 \rightleftharpoons CH_3{\cdot}\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{C}} + HO{\cdot}CH_3.$$

The latter is attributed to the formation, by a similar ionic mechanism, of an intermediate aldehyde form of the sugar; but as this is not necessarily hydrated, it may be produced by isomeric change without addition of water. Since the hydroxyl ion does not then play any essential part in this change, the proton transfer ("prototropic change") can proceed in any medium which is capable of (1) accepting a proton from one part (OH group) of the sugar molecule, and (2) giving a proton to another part (C–O–C group). Regarding an acid as a "proton donator" and a base as a "proton acceptor," an effective solvent for mutarotation should thus be amphoteric in character, *e.g.*, water; acidic and basic solvents should be effective only in the presence of water, or of each other if water is absent. This view has received striking experimental support.[65] In general, pure, dry, neutral solvents are ineffective, whilst pyridine and cresol, ineffective when dry, become active in the presence of water, and develop great catalytic activity when mixed in the *dry* state. The "hydrocatalysis" theory has thus been not only maintained but extended.

H. von Euler's theory of ester hydrolysis, referred to above, has been applied to the mutarotation of glucose.[66] The U-shaped k–p_H curve is nearly symmetrical, with a shallow minimum at the

[65] T. M. Lowry and I. J. Faulkner, *J.*, 1925, **127**, 2883; **A.**, 1926, 148.

[66] Refs. (58), (59), (61); H. von Euler, A. Ölander, and E. Rudberg, *Z. anorg. Chem.*, 1925, **146**, 45; *A.*, 1925, ii, 876; H. von Euler and A. Ölander, *ibid.*, 1926, **152**, 113; **A.**, 580.

isoelectric point p_H 5; k changes little between p_H 2 and p_H 8. The two dissociation constants of the amphoteric sugar are of the order $K_a = 10^{-13}$, $K_b = 10^{-18}$, whence can be calculated the concentration of sugar anions and cations to which the rate is proportional; between p_H 2 and p_H 8 the determining factor is regarded as a function of the zwitterions or neutral molecules. Equation (4) reproduces the experimental data.[67] The nearly-equal slope of the two arms of the curve indicates approximately equal reactivity of the two sugar ions, $k_{cat.}$ and $k_{an.}$ being at least 1000 times greater than k_0. R. Kuhn and P. Jacob [68] are in general agreement with von Euler, but, from a study of salt action, they believe that the velocity of mutarotation depends on activity rather than on concentration of the reactants, and they therefore find evidence for the conclusions of Baker, Ingold, and Thorpe in the fact that the velocity remains unchanged in solutions varying from 2%—50% of sugar in spite of a 20% change in the activity of water. In this connexion, it may be noted that G. G. Jones and T. M. Lowry [69] find no relation whatever between the velocity of mutarotation of tetramethyl glucose in water–acetone mixtures and the aqueous vapour pressure of such mixtures; they conclude that the catalytic effect of water is proportional neither to its concentration nor to its activity.

Optical Activity.

In the last Report on this subject,[1] prominence was given to criticisms of T. M. Lowry's well-known system of classifying rotatory dispersion as "simple" or "complex," according as it can or cannot be expressed by a one-term Drude equation. The system was regarded as lacking justification on practical as well as theoretical grounds, and a return to the older classification into "normal" and "anomalous" rotatory dispersion was considered desirable. These conclusions were largely based on H. Hunter's [2] examination of the two-term Drude formula $\alpha = k_0/(\lambda^2 - \lambda_0^2) + k_1/(\lambda^2 - \lambda_1^2)$, which indicated that a sharp distinction between simple and complex rotatory dispersion would be difficult, except when the complex dispersion was also anomalous, and impossible if the component partial rotations of the complex dispersion were of similar sign.[3] Recent work has, however, proved that the difficulties in the

[67] C. S. Hudson's empirical formula is thus given a theoretical significance; *J. Amer. Chem. Soc.*, 1907, **29**, 1572; *A.*, 1907, ii, 942.

[68] *Z. physikal. Chem.*, 1924, **113**, 389; *A.*, 1925, ii, 49.

[69] *J.*, 1926, 720; **A.**, 481.

[1] *Ann. Report*, 1924, **21**, 3, 61.

[2] *J.*, 1924, **125**, 1198; *A.*, 1924, ii, 645.

[3] "In practice it will be impossible to detect the departure of the $1/\alpha - \lambda^2$ curve from linearity when k_0 and k_1 are both positive. If the rotation constants are of opposite sign, and if $k_0 > k_1$ when $\lambda_0 > \lambda_1$ detection will be possible

practical application of Lowry's system are by no means so great as Hunter suggested. Complex rotatory dispersion was easily demonstrated in ten halogen derivatives of camphor,[4] although only one of them showed anomalous dispersion. With one exception (where a more complex equation was required), all these dispersions could be represented by two-term equations, the terms being of similar sign in three cases and of opposite sign in the others; but only in one case were the conditions fulfilled that the rotation constants should be opposite in sign and $k_0 < k_1$ when $\lambda_0 > \lambda_1$.[3] Further, the undesirability for practical reasons of abandoning the classification of rotatory dispersion as simple and complex, in favour of the normal and anomalous grouping, is evident from the consideration that, in critical cases, the latter depends on knowing whether a reversal of sign would occur if the dispersion-curve could be followed into the infra-red region (usually impracticable at present), whilst the former can be checked by direct observation up to the limit of transparency in the ultra-violet. For example, the rotatory dispersion of β-bromocamphor is complex but normal,[5] since $k_0 > k_1$ when $\lambda_0 > \lambda_1$, but the margin is so narrow that the calculated curve only just fails to cross the λ-axis (*i.e.*, α just fails to suffer reversal of sign); any doubt as to the validity of the equation would at once make the extrapolation into the infra-red region so uncertain that it would be impossible to decide whether the rotatory dispersion were normal or anomalous.[6] As a practical, and in the first place empirical, method of classification, Lowry's system seems to be justified.

The question of its theoretical significance as distinct from its practical utility [7] has been recognised in the attempts to correlate [8]

---

only in very rare cases. The only condition under which the experimental data can be expected to show the effect which Lowry and Dickson regard as evidence of " complex " dispersion is when the rotation constants are opposite in sign and $k_0 < k_1$ when $\lambda_0 > \lambda_1$." (*Ann. Report*, 1924, **21**, 3.)

[4] J. O. Cutter, H. Burgess, and T. M. Lowry, *J.*, 1925, **127**, 1260; *A.*, 1925, ii, 743. For other examples see E. M. Richards and T. M. Lowry, *ibid.*, p. 1512; *A.*, 1925, ii, 934.

[5] T. M. Lowry and J. O. Cutter, *ibid.*, pp. 606, 608; *A.*, 1925, ii, 356.

[6] T. M. Lowry has introduced the term " quasi-anomalous " to describe cases of " complex but normal " rotatory dispersion (*e.g.*, camphor), in which although k_0 and k_1 are of opposite sign, the resulting dispersion-curve shows no obvious anomalies, merely because the relative magnitudes of k_0 and k_1 are not such as to give rise to a reversal of sign. See ref. (5), p. 608; T. M. Lowry, *J. Chim. physique*, 1926, **23**, 565; *Nature*, 1926, **117**, 274.

[7] T. M. Lowry and E. M. Richards, *J.*, 1924, **125**, 2511; *A.*, 1925, ii, 265 (a reply to Hunter's criticisms and a discussion of the practical and theoretical justification of the use of the Drude formula).

[8] See R. H. Pickard and H. Hunter, *ibid.*, 1923, **123**, 435, and *Ann. Report*, 1923, **20**, 15 *et seq.*

the wave length λ_0 of the dispersion constant in the Drude formula (as determined from rotatory-dispersion measurements only) with that of the head of the dominant absorption band λ_a. Such a comparison has been made in the case of camphor,[5] camphorquinone,[7] and nine halogeno-[4] and five sulphonic[9] derivatives of camphor; λ_0 always exceeds λ_a by roughly 100—150 Å.U. The discrepancies are, at any rate in part, accounted for by the displacement of λ_a, due to superposition of selective and general absorption, and these results are regarded as affording some justification for the use of the Drude formula from the *theoretical* standpoint, since, according to the theory λ_0 represents the wave-length of the band controlling rotatory dispersion.[8]

A summary and discussion of the types of optical superposition, any of which may cause complex or anomalous rotatory dispersion, has been given by T. M. Lowry and J. O. Cutter.[10] Six classes are now distinguished, *viz.*, those of: (*a*) Two separate media; (*b*) two mixed, stable, fluid media; (*c*) two molecular types derived from one optically-active compound, one type being generally that composing the crystal, the other being produced either (i) by polymerisation, dissociation, or isomeric change of the solute, or (ii) by chemical reaction with the solvent; (*d*) radicals of opposite activity in one molecule; (*e*) induced asymmetry of double bonds in an asymmetric molecule; (*f*) possibly two natural frequencies (i) in a single crystal, (ii) in a single molecule. A recent study[4] of the mono- and di-halogeno-substitution products of camphor strongly supports the general validity of the principle of optical superposition, the different asymmetrical centres in a molecule contributing independent partial rotation to the observed total.[11]

E. Darmois,[12] reviewing physical theories of optical rotation, concludes that none of them can explain the considerable effects of solvent, concentration, and temperature, and that physicochemical theories [*e.g.*, of dynamic isomerism, class (*c*) above] provide a satisfactory mechanism. Support for the isomeride theory is found by A. Haller and R. Lucas[13] in the approximate constancy of the ratio $([\alpha]_A - [\alpha]_B)/([\alpha]_A - [\alpha]_C)$ over the range 4358—6708 Å.U. for various derivatives of camphor in five solvents, including phosphoric acid[14] (A, B, and C refer to different solvents). This rule, a consequence of Biot's law of mixtures, is accurately

[9] E. M. Richards and T. M. Lowry, *J.*, 1925, **127**, 1503; *A.*, 1925, ii, 934.

[10] Refs. (5) and (6).

[11] See criticisms by T. S. Patterson, *Nature*, 1926, **117**, 786, and remarks by T. M. Lowry, *ibid.*, p. 787.

[12] *J. Phys. Radium*, 1925, [vi], **6**, 232; *A.*, 1925, ii, 1119.

[13] *Compt. rend.*, 1925, **180**, 1803; R. Lucas, *ibid.*, **181**, 45; *A.*, 1925, ii, 742.

[14] *Idem*, *ibid.*, 1926, **182**, 1022; **A.**, 662.

obeyed when B is a mixture of A and C. Again, the dextrorotation of camphor, less in formic acid than in benzene, becomes a slight lævorotation in concentrated nitric or phosphoric acid, and a strong lævorotation in concentrated sulphuric acid.[15] Camphor is therefore considered to exist in solution as an equilibrium mixture of two forms, α and β, of opposite rotatory power, the two terms of the Drude formula for camphor [5] representing the effects of these isomerides. The approximate agreement of the positive term with the rotation constant for crystalline camphor suggests the identity of the α-isomeride with crystalline camphor, as in the case of tartaric acid.[16] According to L. Longchambon,[17] there is no justification for regarding the Drude terms as characteristic of such α and β isomerides, but R. Lucas [14] maintains that as a first approximation they may be so regarded. It may here be noted that Lowry and his associates have obtained strong evidence that in camphor the superposed optical effects are (1) that of the fixed asymmetry of the saturated carbon atoms, and (2) that of the induced asymmetry of the ketonic group, since in most camphor derivatives the positive partial rotation is controlled by a dispersion constant corresponding approximately with the wave-length of the ketonic absorption band.[5]

T. M. Lowry and W. R. C. Coode-Adams [18] have measured with the greatest possible accuracy the rotatory power from infra-red to ultra-violet (25170—2263 Å.U.) of a quartz column nearly 50 cm. long. The dispersion formula

$$\alpha = \frac{9{\cdot}5639}{\lambda^2 - 0{\cdot}0127493} - \frac{2{\cdot}3113}{\lambda^2 - 0{\cdot}000974} - 0{\cdot}1905,$$

which is valid for the whole range, postulates the existence of bands of selective absorption at 1130 and 310 Å.U., the influence of infra-red bands being covered by the small constant, — 0·1905.

In spite of numerous attempts to find a general physical theory of optical activity which can be experimentally tested, it cannot be said that any great success has yet been attained. The incorporation by Drude of a rotation term in his theory of dispersion necessarily provided for optical rotation, but no real explanation of the phenomenon was thereby afforded.[12] Further, the theory took no account of solvent and concentration effects. The latter were associated with the refractive index of the medium in the Lorentz–Livens theory, which, however, did not explain the con-

[15] R. Lucas, *Compt. rend.*, 1926, **182**, 378; **A.**, 337.
[16] *Ann. Report*, 1924, **21**, 59.
[17] *Compt. rend.*, 1926, **182**, 769; **A.**, 559.
[18] *Roy. Soc.*, Dec., 1926 (in press); *Nature*, 1926, **118**, 861.

nexion between rotation and molecular asymmetry. The later theories of M. Born,[19] C. W. Oseen,[20] F. Gray,[21] and A. Landé [22] were, on the other hand, definitely based on molecular asymmetry; they agree broadly in ascribing rotation to unsymmetrically-disposed electron resonators coupled together, *i.e.*, reacting by mutual induction. The relations obtained are complex and do not permit of estimating the order of magnitude of the effect. (Sir) J. J. Thomson's theory,[23] although physically and mathematically simpler, involves molecular magnitudes at present unknown.

A new attack on this problem has recently been made by R. de Mallemann,[24] who has extended the ordinary dispersion formulæ by the introduction of the single notion of molecular asymmetry; his analysis involves the orientation theory put forward by Langevin in connexion with the Kerr effect. The problem of calculating optical rotation appears thus to have been brought appreciably nearer solution. The rotation calculated for a tetrahedral molecule of the type CHClBrI is of the right general order of magnitude, which is all that can be hoped for at present. Complete solution involves a fuller knowledge of molecular structure than we yet possess. Optical rotation, according to this theory, (1) depends on the geometrical form only of the tetrahedron which is determined by the atoms at the apices (the analysis does not call for knowledge of the forces producing the structure), (2) is proportional to the product of the refractivities of the four atoms, thus accounting for the known influence of heavy atoms and of double bonds. It appears, further, that as regards rotation an asymmetric group of atoms behaves almost independently of the rest of the molecule. The analysis indicates great sensitiveness of optical rotation to molecular structure, so that failure to express the experimental variations by any simple law is not surprising.

*Electrification at Surfaces.**

It has long been realised that the Helmholtz conception of the electrical double layer at surfaces as two layers of ions of opposite charges confronting each other at a fixed distance (condenser

[19] *Ann. Physik*, 1918, [iv], **55**, 177; *A.*, 1918, ii, 283.
[20] *Ibid.*, 1915, **48**, 1.
[21] *Physical Rev.*, (2), 1916, **7**, 472.
[22] *Ann. Physik*, 1918, **56**, 225; *Physikal. Z.*, 1918, **19**, 300.
[23] *Phil. Mag.*, 1920, [vi], **40**, 713.
[24] *Ann. Physique*, 1924, [x], **2**, 5; 1925, [x], **4**, 456; *A.*, 1925, ii, 1029; *Compt. rend.*, 1923, **177**, 427; 1925, **181**, 106, 298, 371; *A.*, 1925, ii, 840, 935, 1030. See also ref. (12).

* See the Faraday Society's discussion on electrification at surfaces (*Trans. Faraday Soc.*, 1926, **22**, 434). Some of the papers contributed are referred to below.

fashion) is inadequate. J. Billiter [1] and G. Gouy [2] suggested that ions in the liquid form a diffuse layer. D. L. Chapman [3] applied the Boltzmann equation to obtain the distribution of ions in a diffuse layer, but his equations have been shown to be inadequate.[4] O. Stern [5] has therefore postulated a combination of the two types—a " condensed " double layer near the surface of separation; beyond it, in the liquid, a " diffuse " layer of ions.

The " thermodynamical " potential difference (ϵ) measured across the surface is the total *P.D.* due to both layers. On the other hand, electrokinetic measurements give the *P.D.* (ζ) across that part of the interface which is capable of displacement parallel to the surface, *i.e.*, the " diffuse " layer. The two *P.D.*'s have been measured by H. Freundlich and co-workers,[6] at glass surfaces in a variety of solutions. Not only do they differ, but they may be of opposite sign. Whilst the ϵ *P.D.* is not much influenced by the salt concentration, the ζ–*c* curves are very characteristic for salts of different types. There is no satisfactory theory of the relation between ζ and ϵ, since Stern's equation cannot be applied to actual cases.

H. Lachs and J. Kronman,[7] however, find that these potentials can only be reproduced within 14%. It is to be expected that only *P.D.*'s which depend on a thermodynamical equilibrium between the two phases are definite and reproducible (thus a metal only gives a definite *P.D.* in solution containing its ions), and the above cases do not come within this category. Measurements of ϵ and ζ at the surfaces of slightly soluble salts and solutions containing their ions are therefore of greater value. A. Gyemant [8] has made such measurements with barium sulphate, and R. Labes [9] with barium sulphate, zinc oxalate, lead chromate, and silver

[1] *Z. physikal. Chem.*, 1903, **45**, 307; *A.*, 1904, ii, 18.

[2] *J. Physique*, 1910, [iv], **9**, 457; *Ann. Physique*, 1917, [ix], **7**, 129; *A.*, 1917, ii, 291.

[3] *Phil. Mag.*, 1913, [vi], **25**, 475. Also K. F. Herzfeld, *Physikal. Z.*, 1920, **21**, 28.

[4] A. Frumkin, *Phil. Mag.*, 1920, [vi], **40**, 375; *A.*, 1920, ii, 578; O. K. Rice, *J. Physical Chem.*, 1926, **30**, 1501.

[5] *Z. Elektrochem.*, 1924, **30**, 508.

[6] H. Freundlich and P. Rona, *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1920, **20**, 397; H. Freundlich and G. Ettisch, *Z. physikal. Chem.*, 1925, **116**, 401; *A.*, 1925, ii, 873. Summary of results by H. Freundlich, *Trans. Faraday Soc.*, 1926, **22**, 440.

[7] *Bull. Int. Acad. Polonaise*, 1925, *A*, 289; **A.**, 1926, 803.

[8] *Z. physikal. Chem.*, 1922, **103**, 260; *A.*, 1923, ii, 52. The ϵ *P.D.* between solid salts and their solutions was first realised by F. Haber, *Ann. Physik*, 1908, [iv], **26**, 927; *A.*, 1908, ii, 802. A. Gyemant has discussed the theory of ionic adsorption applied to such cases, *Z. physikal. Chem.*, 1924, **108**, 387; *A.*, 1924, ii, 391.

[9] *Ibid.*, 1925, **116**, 1; *A.*, 1925, ii, 796.

chloride. The latter has worked out a detailed theory. Since ions of opposite charge to the solid accumulate near the surface—and to a greater extent the greater their concentration in the solution—the electrokinetic potential is small in concentrated solutions. In more dilute solutions, specific effects are observable, and in the absence of specific adsorption of ions, the theory indicates that an ion influences the electrokinetic potential the more the smaller the solubility product of the salt which it forms with either of the component ions of the solid. This conclusion is confirmed by the experiments.

A. Frumkin and associates have made measurements of the *P.D.* at the surface of aqueous solutions by F. B. Kenrick's method,[10] in which the *P.D.* is measured between the solution flowing down the inside wall of a cylindrical tube and a stream of a standard solution flowing down its axis. In salt solutions,[11] the outer surface is in nearly all cases negatively charged; the predominance of anions, thus indicated near the surface, is greater the less their energy of hydration, and the effect on the *P.D.* is in the same order. Similar measurements have been made with organic compounds. The results are in accordance with the orientation of molecules in the surface layer, and give valuable information as to their polarity. Aliphatic alcohols, esters, amines, etc.,[12] increase the positiveness of the surface owing to their orientation with the relatively positive alkyl groups outwards. Strong acids and neutral salts have the opposite effect, owing to the greater attraction of water for cations than for the carboxyl group. I. Traube's adsorption rule (*viz.*, that as the number of methyl groups increases in arithmetical progression, the adsorption from solutions of the same concentration increases roughly in geometrical progression) holds also for these *P.D.*'s. Aromatic compounds show similar relations.[13] The effect of methyl groups is, however, less than in aliphatic compounds and the presence of polar groups in the nucleus may reverse the effect.

This method is only applicable when the surface equilibrium is quickly reached. A method has been devised [14] for use with

[10] *Z. physikal. Chem.*, 1896, **19**, 625; *A.*, 1896, ii, 460.

[11] A. Frumkin, *ibid.*, 1924, **109**, 34; *A.*, 1924, ii, 462. Compare A. Frumkin, S. Reichstein and R. Kulvarskaya, *Kolloid Z.*, 1926, **40**, 9; **A.**, 1091. A. Frumkin and A. Donde (*Z. physikal. Chem.*, 1926, **123**, 339; **A.**, 1104) find that mercury can be substituted for the standard solution.

[12] A. Frumkin, *ibid.*, 1924, **111**, 190; *A.*, 1925, ii, 109.

[13] A. Frumkin, A. Donde and R. Kulvarskaya, *ibid.*, 1926, **123**, 321; **A.**, 1092.

[14] A. Frumkin, *ibid.*, 1925, **116**, 485; *A.*, 1925, ii, 873; *Kolloid Z.*, 1924, **35**, 340; *A.*, 1925, ii, 544; *Trans. Karpov. Inst. Chem.* [*Russia*], 1925, No. 4, 56; **A.**, 1926, 1093.

solutions giving insoluble unimolecular films, in which the *P.D.* is measured between the stationary solution and either a glowing wire or a wire containing some radioactive material, in order to make the air-gap sufficiently conducting. In these cases, the *P.D.* is proportional to the amount adsorbed until a complete unimolecular layer is formed, after which it remains constant.

W. Wessel [15] has worked out an elaborate statistical theory of the surface charges of inorganic electrolyte solutions, and is able to account for Frumkin's results. A. Garrison [16] has used a condenser method to determine the surface charges of electrolytes. R. D. Kleeman and C. R. Pitts [17] have also studied the sign of the charge furthest from the solution by another method. H. W. Gilbert and P. E. Shaw [18] have recently summarised the literature on the determination of electric charges at gas–liquid interfaces.

The study of the surface phenomena of mercury in electrolytic solutions promises to give particularly valuable information about electrification at surfaces and also about the effect of an electric field on the constituents of the solution, for it is the unique case in which the *P.D.* can be varied at will by polarisation and the effects on the surface tension observed at the same time. The classical equation of Gibbs and Helmholtz, $d\gamma/dV = -e$, which equates the rate of change of surface tension with applied *P.D.* to the charge on the double layer e, has been obtained in numerous ways. R. K. Schofield [19] has identified e with the amount of adsorbed mercury ions and has directly determined this amount by an ingenious method, obtaining results in good agreement with the equation.[19a] A. Frumkin [20] has discussed the effect of the adsorption of anions and cations and of neutral capillary-active substances on the electro-capillary curve. In the latter case, variations of surface tension are given by $d\gamma = -e \,.\, dV - \Sigma\Gamma_A d\mu_A$. The first term on the right represents the effect of electrification, the second (in which Γ_A is the amount of adsorbed substance A, and μ_A its chemical potential in the solution) the lowering of surface tension produced by the capillary-active substance. Since Γ_A is itself a

[15] *Ann. Physik*, 1925, [iv], **77**, 21; *A.*, 1925, ii, 795.

[16] *J. Physical Chem.*, 1925, **29**, 1517; **A.**, 1926, 130.

[17] *Ibid.*, p. 508; *A.*, 1925, ii, 659.

[18] *Proc. Physical Soc.*, 1925, **37**, 195; *A.*, 1925, ii, 795.

[19] *Phil. Mag.*, 1926, [vii], **1**, 641; **A.**, 572; *Trans. Faraday Soc.*, 1926, **22**, 452. Compare A. Frumkin, *Z. physikal. Chem.*, 1922, **103**, 55; *A.*, 1923, ii, 54.

[19a] W. A. Patrick and P. W. Bachman (*J. Physical Chem.*, 1926, **30**, 134; **A.**, 239) and J. E. Rosenburg and G. Stegeman (*ibid.*, p. 1306; **A.**, 1201) also have investigated the adsorption of ions at the mercury surface.

[20] *Phil. Mag.*, 1920, [vi], **40**, 363, 375; *A.*, 1920, ii, 578; also ref. (19).

function of V, this equation does not give the complete variation of γ with V. Frumkin [21] has applied the equation $\Delta\gamma = A \log (Bc+1)$ for the lowering of surface tension produced by an active substance and has obtained B as a function of the electric-field strength in the form $B = B_0 e^{\phi s/RT}$, where ϕs is the additional electrical work of adsorption due to the electric field. On this basis, the effect of amyl alcohol on the electro-capillary curve is satisfactorily accounted for. Capillary-active neutral substances in general only lower the surface tension in the vicinity of the electro-capillary maximum, *i.e.*, when the electric field strength is low. The amount adsorbed is therefore diminished by increasing the *P.D.* at the interface in either direction. It has been found by direct measurement [22] that the adsorption of *n*-octoic acid at the surface of silver iodide increases to a sharp maximum at about the isoelectric point.

O. K. Rice [23] has investigated the surface tension of charged surfaces, obtaining the expression $d\gamma/dV = -e - \Sigma\Gamma_i d\mu_i/dV$, in which the second term represents the effect of the adsorption of ions (μ_i is the chemical potential in the superficial layer of ions of the ith kind). These terms are interpreted from the point of view of electrostatic theory. A detailed analysis of the changes produced by electrolytic polarisation at the mercury surface and the thermodynamical theory of their effects on the surface tension has been given by J. A. V. Butler.[24] It is held that Gibbs's equation by itself is inadequate to account for the electrocapillary curves, an electrostatic effect in addition having to be taken into account. The following equation is obtained,

$$d\gamma/dV = -2e - a_{\mathrm{Hg}^{\cdot}}\Gamma_{\mathrm{Hg}^{\cdot}} - \Sigma d\{\Gamma_x d\mu_x\}/dV,$$

in which the first term represents the electrostatic effect, the second the effect of adsorbed mercury ions, the third the effect of other adsorbed ions or molecules. In the third term Γ_x itself varies with V, and this variation can only be calculated by kinetic methods. An application of the theory of ionic adsorption is outlined which accounts quantitatively for the electro-capillary curves in iodide solutions and is capable of accounting qualitatively for all types of curves exhibited by salt solutions.

O. K. Rice [25] has examined the application of various theories of the electrolytic double layer to the electro-capillary curves. Chapman's equation [26] is inadequate. As an alternative to Stern's

[21] *Z. Physik*, 1926, **35**, 792; **A.**, 347.
[22] A. Frumkin and A. Obrutshewa, *Nature*, 1926, **117**, 790; **A.**, 674.
[23] *J. Physical Chem.*, 1926, **30**, 1348; **A.**, 1202.
[24] *Proc. Roy. Soc.*, 1927, [*A*], **113**, 594.
[25] *J. Physical Chem.*, 1926, **30**, 1501.
[26] Compare ref. (3).

theory of a "condensed" double layer at the surface and a diffuse layer in the solution, it is suggested that the electronic charge in the mercury may not reside entirely at the surface but may also be diffuse. The two assumptions give very similar results but are not entirely adequate. E. Liebreich [27] has put forward evidence for the belief that the maximum of the electro-capillary curve corresponds with the formation of hydroxide or basic salt on the surface of the mercury by cathodic polarisation. F. L. Usher [28] has examined electro-capillary curves in salt solutions in connexion with the electrokinetic behaviour.

J E. Coates.
J. A. V. Butler.

[27] *Z. Elektrochem.*, 1926, **32**, 162; **A.**, 478. Compare E. Liebreich and W. Wiederholt, *ibid.*, 1924, **30**, 263; *A.*, 1925, ii, 44.
[28] *J. Physical Chem.*, 1926, **30**, 954; **A.**, 803.

INORGANIC CHEMISTRY.

The Report for 1926 has been prepared in the same manner as previous Reports and, to save space, the reader's attention may be directed to the remarks prefacing the Report for 1925, which are applicable to this one also.

Among subjects which appear to be of special interest are several cases of apparent transmutation of elements (hydrogen to helium, mercury to gold, lead to mercury and thallium), further work on the hydrides of boron, the discovery of the missing rare-earth element (No. 61) "illinium," and a good deal of work on the effects of intensive drying, noted in several parts of the Report.

Atomic Weights.

Helium. The technique previously developed for determining the density of oxygen has been applied to determine the normal density of helium. The value obtained is 0·17846 at 0° and 760 mm. at sea level in latitude 45°, g being taken as 980·398. Hence the atomic weight of helium is 4·000 with an experimental error affecting the 4th decimal only.[1]

Boron. A flotation method has been utilised to compare the densities of samples of boric oxide prepared from six boron minerals from different parts of the world. The boric oxide beads were sealed in glass tubes with the same mixture of dry, inert, organic liquids of known density, and the temperature of flotation of the beads in each sample was then observed. The mean density of fused boric acid at 18° is 1·7952. The densities of the several samples varied from 1·79711 to 1·79404, indicating variations in the atomic weight of boron from 10·847 to 10·788. The three samples for which previous determinations of the ratio $BCl_3 : 3Ag$ had given the values 10·841, 10·825, and 18·818, gave relative values deduced from the densities 10·847, 10·823, and 10·818.[2]

Silicon. A similar flotation method, using glass floats of appropriate density, previously calibrated by determination of their flotation temperatures in a mixture of organic liquids of known density, has been applied to compare the densities of, and hence the

[1] G. P. Baxter and H. W. Starkweather, *Proc. Nat. Acad. Sci.*, 1925, **11**, 231; 1926, **12**, 20; *A.*, 1925, ii, 1045; **A.**, 1926, 233.

[2] H. V. A. Briscoe, P. L. Robinson, and G. E. Stephenson, *J.*, 1926, 70; **A.**, 219; compare *Ann. Reports*, 1925, **22**, 43.

atomic weights of the samples of silicon in, preparations of silicon tetrachloride derived from five precisely known localities in Canada, the United States, Sweden, Scotland, and France, and subjected to a rigorous purification by fractional distillation under exclusion of moisture, first at atmospheric pressure and afterwards in a vacuum. The extreme values for the atomic weight of silicon deduced from the densities of silicon tetrachloride are 28·058 and 28·063, the maximum variation thus being one part in 6000 parts, and the probable error of individual relative values of the atomic weight considerably less than this. These results are held to show that any variation in the atomic weight of silicon from different sources is substantially less than one unit in the second decimal place,[3] and confirm and extend the conclusion deduced from pyknometric measurements of the density of tetraethylsilicane by Jaeger and Dijkstra.[4]

Chlorine. Determinations are recorded of the ratio AgCl : Ag, using samples of chlorine derived from the sea, from three minerals of non-marine origin, *viz.*, apatite, wernerite, and sodalite, and from a meteorite. The mean value of the atomic weight for chlorine in common salt and the three terrestrial minerals is $35{\cdot}457 \pm 0{\cdot}0002$, whilst that of the meteoritic chlorine is $35{\cdot}458 \pm 0{\cdot}0005$. These determinations afford further evidence, much more precise than that hitherto available, that the atomic weight of chlorine does not vary with its source.[5]

Germanium. Metallic germanium derived from the germanium tetrachloride previously used for atomic-weight determinations,[6] was converted into germanium tetrabromide, and this compound, after purification by 13 fractional distillations in a vacuum, was used for determinations of the ratios $GeBr_4 : 4Ag$, $GeBr_4 : 4AgBr$. The mean of 32 analyses gave Ge = 72·60, a value identical with that given by analysis of the tetrachloride.[7]

Silver. A thorough investigation has shown that silver oxide is much more stable than has hitherto been supposed, and that, when it is prepared by precipitating silver nitrate with baryta under rigid exclusion of organic matter and carbon dioxide, it may be

[3] P. L. Robinson and H. C. Smith, *Nature*, 1926, **118**, 303; **A.**, 999; *J.*, 1926, 1262; **A.**, 771; H. V. A. Briscoe and P. L. Robinson, *Nature*, 1926, **117**, 377; **A.**, 331.

[4] F. M. Jaeger, *Z. Elektrochem.*, 1926, **32**, 328; **A.**, 879; compare *Ann. Reports*, 1925, **22**, 44.

[5] W. D. Harkins and S. B. Stone, *J. Amer. Chem. Soc.*, 1926, **48**, 938; **A.**, 553.

[6] *Ann. Reports*, 1924, **21**, 28.

[7] G. P. Baxter and W. C. Cooper, *J. Physical Chem.*, 1925, **29**, 1364; **A.**, 1926, 5.

heated in a current of pure air at 120° for a week without decomposition, and thereafter will yield a white chloride on treatment with hydrochloric acid. By heating pure silver oxide thus prepared in a silica tube at 350—400°, in a current of pure dry air, 6 direct determinations were made of the ratio $Ag_2O : Ag$, giving a mean value for the atomic weight of silver Ag = 107·864 ± 0·0013. The original paper must be consulted for interesting details of the preliminary investigation into the stability of silver oxide and of the apparatus and methods used in the actual determinations.[8] Nine determinations of the silver remaining after ignition of silver carbonate, prepared and dried under the conditions found to give a minimum of decomposition, gave a mean value for the atomic weight of silver Ag = 107·86.[9]

Lead. In the course of unsuccessful attempts to obtain some separation of the isotopes present in ordinary lead by irreversible volatilisation and by the Grignard process, 18 values for the ratio $PbCl_2 : 2Ag$ were obtained, giving a mean value for the atomic weight of lead Pb = 207·217 ± <0·001.[10]

Four determinations of the ratio $PbCl_2 : 2Ag$ upon lead extracted from a specimen of uraninite from the Black Hills, South Dakota, gave a mean value for the atomic weight of lead Pb = 206·07. When a correction is applied for the known thorium content of the mineral, it appears that the atomic weight of uranium–lead in this specimen is Pb = 206·02. It is of interest that the high lead–uranium ratio, 0·23, of this relatively pure uranium–lead indicates an age for the mineral of at least 1500 million years.[11]

Titanium. In continuation of work previously reported, 17 determinations of the ratio $TiCl_4 : 4Ag$, made on material from the later stages of the fractionation of the tetrachloride, yielded results for the atomic weight of titanium lying within the limits 47·883—47·922 and giving the mean value Ti = 47·90.[11a]

Group O.

A development in the methods of detecting helium has afforded evidence of the production of that gas from hydrogen. By removing the relatively condensable gases with charcoal and liquid air, burning hydrogen with excess of oxygen on a platinum or palladium catalyst, absorbing the residual oxygen with charcoal, and examining

[8] H. L. Riley and H. B. Baker, *J.*, 1926, 2510; **A.**, 1190.

[9] G. H. Jeffrey and A. W. Warrington, *Chem. News*, 1926, **132**, 373; **A.**, 694.

[10] T. W. Richards, H. S. King, and L. P. Hall, *J. Amer. Chem. Soc.*, 1926, **48**, 1530; **A.**, 771.

[11] T. W. Richards and L. P. Hall, *ibid.*, p. 704; **A.**, 449.

[11a] G. P. Baxter and A. Q. Butler, *ibid.*, p. 3117; compare *Ann. Reports*, 1923, **20**, 30.

the residual gas spectroscopically in a minute glass capillary, it is possible to detect quantities of helium as small as 10^{-8} or 10^{-9} c.c. and thus to detect the gas evolved from active thorium precipitates, and determine the quantity in quite small samples of natural gas. When hydrogen free from helium is passed over heated palladium, the issuing gas is found to contain helium, and the quantity of helium appears to be increased when the hydrogen is allowed to remain in contact with palladium-black, spongy palladium, or palladised asbestos at the ordinary temperature. Although the behaviour of the catalyst is somewhat irregular, and its activity diminishes with time, there is a rough proportionality between the duration of contact of the hydrogen with the metal and the quantity of helium found thereafter. Catalysts inactive to hydrogen, and occasionally catalysts which readily absorb hydrogen, do not yield helium, but, in general, a catalyst active towards hydrogen does produce helium. A catalyst which has become inert may be revived in the usual manner, and may then produce helium. Specimens of finely-divided palladium which have been preserved for a time at the ordinary temperature always yield helium on heating. There is, of course, some neon in this gas, but the ratio of helium to neon is usually much greater than that in air. These observations all lead to the conclusion that the palladium in this case acts purely as a catalyst for the conversion of hydrogen into helium, and this view is confirmed by the further observation that a similar, although less, effect is produced by platinum.[12]

Measurements of the surface tension of liquid helium in contact with its saturated vapour by the method of capillary rise have shown that the molecular surface tension increases linearly with fall of temperature down to 2·4° Abs., and thereafter approaches a constant value in the neighbourhood of 1·5° Abs.[13] By observing the absolute temperatures and pressures at which a tube system, containing liquid helium, became blocked, it has been inferred that the fusion curve of helium is described by the following points : 1·1°, 2·6 atm.; 2·2°, 50 atm.; 3·2°, 86 atm.; 4·2°, 150 atm. When helium was frozen in a glass tube, no boundary surface was visible between the solid and liquid phases, whence it appears that the refractive indices of solid and liquid helium must be closely similar.[14] It has been shown that quartz glass is permeable to helium under a pressure of 100 atm. at laboratory temperatures, whereas under the same experimental conditions no permeability to hydrogen could be detected.[15]

[12] F. Paneth and K. Peters, *Ber.*, 1926, **59**, [*B*], 2039; **A.**, 1077.

[13] A. T. van Urk, W. H. Keesom, and H. K. Onnes, *Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 958; **A.**, 1926, 568.

[14] W. H. Keesom, *Compt. rend.*, 1926, **183**, 26, 189; **A.**, 892, 893.

[15] H. M. Elsey, *J. Amer. Chem. Soc.*, 1926, **48**, 1600; **A.**, 895.

Group I.

Some interesting work is reported on the reduction of aqueous solutions of metallic salts by hydrogen under pressure. With solutions containing 3—30% of platinum chloride, the yield of platinum in unit time increases with temperature and with pressure of hydrogen, whilst the proportion of the total platinum precipitated increases with diminishing initial concentration of the solution. Presence of iron and nickel salts and mineral acids greatly retards or inhibits the reduction.[16] The action of compressed hydrogen on hot copper sulphate solution yields, first the basic salt $CuSO_4,2Cu(OH)_2$, then cuprous oxide, and ultimately copper, the quantity of which increases with the amount of free sulphuric acid present. At 150°, there is some reduction of sulphuric acid and this facilitates the separation of basic salts and cuprous oxide; at higher temperatures copper sulphide is produced. This reduction of sulphuric acid is accelerated by the precipitated copper. Chromic acid, alone or in the presence of sulphuric acid, is reduced to the oxide, Cr_2O_3,H_2O; whilst potassium dichromate, acidified with sulphuric acid, at 300° and 80 atm. of hydrogen, yields small violet-grey crystals of a *salt*, $K_2O,2Cr_2O_3,3SO_3,H_2O$, insoluble in acid or alkali. From nickel formate, under relatively drastic conditions, anhydrous, crystalline *nickelous oxide* is produced; lower temperatures and pressures give a quantitative yield of metallic nickel. Phosphoric acid is not reduced at 350°, but lead hydrogen orthophosphate is reduced to lead hydrogen phosphite, hypophosphorous acid, and colloidal lead oxide. Red phosphorus at 200° and 90 atm. is converted into black phosphorus, but under milder conditions it yields phosphine and phosphoric acid. Many other interesting reactions are described in the original papers.[17]

A good deal of evidence converges on the view that many of the so-called metallic hydrides are in fact not stoicheiometric compounds but solid solutions approximating closely thereto. Even calcium hydride, usually regarded as a typical salt-like hydride of the type formed by the alkali and alkaline-earth metals, is found to contain less hydrogen than is required by the formula CaH_2, and to show, even at 20°, a measurable hydrogen pressure, steadily increasing with time, even after 9 days. On removing hydrogen from calcium hydride, the substance slowly separates into two portions, one approximating closely to CaH_2, the other poorer in hydrogen. Similarly, it is found that dry copper hydride always contains less hydrogen than is required by the formula CuH and loses hydrogen

[16] V. Ipatiev and A. Andreevski, *Compt. rend.*, 1926, **183**, 51; **A.**, 921.

[17] V. Ipatiev and others, *Ber.*, 1926, **59**, [*B*], 1412; **A.**, 921; V. N. Ipatiev and B. A. Mouromtsev, *Compt. rend.*, 1926, **183**, 505; **A.**, 1114.

progressively when heated.[18] Observations on the absorption of hydrogen by praseodymium, neodymium, zirconium, and thorium, and on the dissociation of the products, indicate that these hydrides also, as well as those of cerium and lanthanum, are solid solutions which, under favourable conditions, may approximate to, but never actually attain, the composition and stability of stoicheiometric compounds.[19]

A thorough investigation of the action of copper on concentrated sulphuric acid has shown that whilst at all temperatures from 16° to 270° the completed reaction is represented by the equation $Cu + 2H_2SO_4 \longrightarrow SO_2 + CuSO_4 + 2H_2O$, there actually occur at least four different reactions :

(i) $5Cu + 4H_2SO_4 = Cu_2S + 3CuSO_4 + 4H_2O$;
(ii) $Cu_2S + 2H_2SO_4 = CuS + CuSO_4 + 2H_2O + SO_2$;
(iii) $CuS + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2 + S$;
(iv) $S + 2H_2SO_4 = 2H_2O + 3SO_2$.

In the temperature range 100—120°, action (i) is much more rapid than actions (ii) and (iii) ; hence sulphide formation is particularly evident. At 270°, actions (ii) and (iii) are so rapid that the presence of sulphides as intermediate compounds is not readily detected. The crystalline deposit formed is anhydrous copper sulphate, which is white when formed at high temperatures, but at lower temperatures is grey, owing to inclusion of black sulphides; microscopic examination of the crystals gave evidence that this salt is dimorphous.[20]

Evidence is adduced that discrepancies in the literature relative to basic copper sulphates are attributable to the formation of highly stable intermediate compounds, and that the basic salt obtained by boiling solutions of copper sulphate for a short time is

$$5CuSO_4,9Cu(OH)_2,2H_2O.$$

This salt can easily be produced in quantity if the acid produced on hydrolysis is removed as it is formed by interaction with sodium nitrite present in the solution. On prolonged boiling with water, this basic salt or copper sulphate yields $CuSO_4,2Cu(OH)_2$. By hydrolysis of copper sulphate in solutions over a small range of concentration near saturation, a new basic salt, $2CuSO_4,Cu(OH)_2,4H_2O$, was obtained which has apparently eluded previous observers owing to its decomposition by water. Two other basic salts, $CuSO_4,3Cu(OH)_2$ and $2CuSO_4,3Cu(OH)_2$, were recognised as definite compounds.

[18] G. F. Hüttig, *Z. angew. Chem.*, 1926, **39**, 67; **A.**, 254; G. F. Hüttig and F. Brodkorb, *Z. anorg. Chem.*, 1926, **153**, 235, 309; **A.**, 694, 809; see also H. Müller and A. J. Bradley, *J.*, 1926, 1670.

[19] A. Sieverts and E. Roell, *ibid.*, **150**, 261; **153**, 289; **A.**, 356, 810.

[20] C. W. Rogers, *J.*, 1926, 254.

The original paper contains a very thorough discussion of the whole literature of the basic copper sulphates in the light of the present work and merits careful study.[21]

Reinvestigation of the cuprous alkali thiosulphates has disclosed the existence of the ammonia compounds $Cu_2S_2O_3,2K_2S_2O_3,NH_3$ and $Cu_2S_2O_3,Na_2S_2O_3,2NH_3$.[22]

Silver perchlorate is unique among typical metallic salts in being readily soluble in toluene, the solution saturated at 25° containing 50·3% of the salt: below 22·6° the solid phase in equilibrium with the solution is $AgClO_4,C_7H_8$, and the solubility falls off rapidly at lower temperatures. These observations are incidental to an examination of the ternary system—silver perchlorate–toluene–water—for the results of which the original paper must be consulted.[23]

Further application of the Steele–Grant microbalance and the methods previously described has shown that optimum concentrations of chlorine exist for the chlorination of both fresh and previously-chlorinated silver films, that photochemical decomposition of silver chloride and silver iodide films may proceed to the extent of 94—95%, and that there is no evidence of the formation of subchloride or subiodide.[24]

Group II.

Compact masses of beryllium have been prepared by electrolysing the double fluoride at 1200° in a graphite pot with graphite anodes previously impregnated with the salt. The rotating cathode has a beryllium tip held in a water-cooled holder and is slowly raised as electrolysis proceeds: thus a solid rod of beryllium is obtained. The crude metal is free from impurities except about 0·05% each of iron, carbon, aluminium, and magnesium and about 0·005% nitrogen; by sublimation in beryllia pots, carbide-free metal containing less than 0·02% iron was obtained. Beryllium has *d* 1·84 and m. p. about 1280°; it takes a high polish, resists atmospheric corrosion well, does not readily ignite, is non-ductile, and has a Brinell hardness usually about 140 but in one annealed sublimate as low as 90.[31]

Investigations of the viscosities of solutions of beryllium sulphate, selenate, and oxalate containing dissolved beryllia, and of the conductivities of neutral and basic solutions of beryllium chloride

[21] G. Fowles, *J.*, 1926, 1845. Compare, however, H. T. S. Britton, *ibid.*, p. 2868.

[22] A. Benrath, H. Niehaus, H. Meckenstock, and H. Essers, *Z. anorg. Chem.*, 1926, **151**, 31; **A.**, 367.

[23] A. E. Hill and F. W. Miller, *J. Amer. Chem. Soc.*, 1925, **47**, 2702; **A.**, 1926, 26.

[24] E. J. Hartung, *J.*, 1925, **127**, 2691; 1926, 1349; compare *Ann. Reports*, 1922, **19**, 43; 1924, **21**, 35.

[31] A. C. Vivian, *Trans. Faraday Soc.*, 1926, **22**, 211; **A.**, 1114.

and oxalate, yield results consistent with the view that the sulphate and selenate solutions contain a complex cation, Be,xBeO, where x on the whole is less than 4. In the course of this work, *beryllium benzenesulphonate* and p-*toluenesulphonate* were obtained as crystalline salts with $4H_2O$.[32]

By using a crucible, stirrer, and thermometer-sheath made of a 5 : 2 mixture of bole and alumina, which softens only at 1560° and is not attacked by the melt, it has been possible to make a thermal analysis of the calcium and magnesium silicides. Two calcium silicides, CaSi, m. p. 1220°, and $CaSi_2$, m. p. 1020°, are formed, and there is some evidence for a third compound, Ca_2Si, m. p. 920°. Both CaSi and $CaSi_2$ are decomposed by water, yielding spontaneously inflammable silicon hydrides. Thermal analysis of magnesium–silicon melts shows only the compound Mg_2Si, m. p. 1070°, already known, but when the melt is rapidly cooled from above 1050°, a second silicide, MgSi, is obtained, which is also formed by volatilisation of magnesium when Mg_2Si is kept at temperatures above 600°. Above 1100°, both silicides dissociate, yielding the elements.[33]

A thermometric study of the setting of plaster of Paris, in which the maximum on the time–temperature curve was taken as the time of setting, shows that setting occurs in two stages: (*a*) a slightly exothermic absorption with contraction in volume, and (*b*) a markedly exothermic reaction between the absorbed liquid and the absorbent with an attendant increase in volume. The accelerating effect of cations in this change is in the order $K > NH_4 > Na > Li$; $Zn = Cu > Mg$: the decelerating effect of anions is in the order $I > NO_3 > Br > Cl$.[34]

Calcium sulphate, on being heated with carbon at 900° or with hydrogen at 600—800°, yields calcium sulphide, but above 900° this product reacts with undecomposed sulphate, yielding lime and sulphur dioxide; at higher temperatures, interaction occurs between carbon monoxide and sulphur dioxide, producing sulphur, with carbon oxysulphide as a by-product.[35] Simple dissociation of calcium sulphate begins at 960° and the dissociation pressure reaches 97 mm. at 1230°; in an equimolecular mixture with amorphous silica, dissociation begins at 870° and produces a pressure of 817 mm.

[32] N. V. Sidgwick and N. B. Lewis, *J.*, 1926, 1287; see general discussion of co-ordinated additive compounds of beryllium, R. Fricke, *Z. angew. Chem.*, 1926, **39**, 317; R. Fricke and O. Rode, *Z. anorg. Chem.*, 1926, **152**, 347; R. Fricke and L. Havestadt, *ibid.*, p. 357; **A.**, 368, 694, 695.

[33] L. Wöhler and O. Schliephake, *ibid.*, 1926, **151**, 1; **A.**, 368.

[34] H. A. Neville, *J. Physical Chem.*, 1926, **30**, 1037; **A.**, 899.

[35] J. Zawadzki, J. Konarzewski, W. J. Lichtenstein, S. Szymankiewicz, and J. Wachsztejński, *Rocz. Chem.*, 1926, **6**, 120, 236; **A.**, 923.

at 1280°. The effect of alumina and ferric oxide has also been studied.[36]

When baryta is heated with cupric sulphide or lead sulphide it brings about a partial reduction to metal (72% in 1 hr. at 1150° in the case of copper) according to the equations of the type :[37]

$$CuS + BaO \longrightarrow CuO + BaS; \quad 4CuO + BaS \longrightarrow BaSO_4 + 4Cu.$$

From a study of the solubility curves and the composition of the solid phases in the system Al_2O_3–BaO–H_2O at 20°, only two barium aluminates could be isolated, *viz.*, $2BaO,Al_2O_3,5H_2O$, stable in solutions containing from 3·5 to 2·1% of barium oxide, and $BaO,Al_2O_3,6H_2O$, stable in concentrations of from 2·1 to 1·2% of barium oxide. Several compounds described in the literature were not obtained. The former compound is rapidly decomposed by water into the latter, which is also decomposed by a large excess of water into barium hydroxide and gelatinous aluminium hydroxide.[38]

The cooling curves of calcium amalgams and their microstructures when frozen on glass surfaces are consistent with the existence of three compounds, $CaHg_3$, $CaHg_5$, and $CaHg_{10}$, and the second of these may be obtained in relatively large crystals by pouring the amalgams into water.[39]

Stock has directed attention to the possibility that workers exposed to the vapour given off by mercury at laboratory temperatures may contract very serious mercury poisoning, unless there is an extremely good system of ventilation. The condition of chronic poisoning thus developed can only be cured by several years' abstention from all work involving the use of mercury. Some workers deny the possibility of such poisoning, but others can confirm Stock's experience.[40] It seems possible that much depends on personal idiosyncrasy, so that, whilst some persons are relatively immune, others may in fact contract chronic mercurial poisoning under ordinary laboratory conditions; if so, a clear case exists for the exercise of greater precaution than has been customary in the use of mercury.

[36] (Mlle.) G. Marchal, *J. Chim. phys.*, 1926, **23**, 38; **A.**, 359; *Bull. Soc. chim.*, 1926, [iv], **39**, 401; **A.**, 487.

[37] W. Biltz and E. von Mühlendahl, *Z. anorg. Chem.*, 1925, **150**, 1; **A.**, 1926, 136; I. A. Hedvall, *Svensk Kem. Tidskr.*, 1925, **37**, 166; from *Chem. Zentr.*, 1925, II, 1946; J. A. Hedvall and E. Norström, *Z. anorg. Chem.*, 1926, **154**, 1; **A.**, 368, 695.

[38] G. Malquori, *Gazzetta*, 1926, **56**, 51; **A.**, 810.

[39] A. Eilert, *Z. anorg. Chem.*, 1926, **151**, 96; **A.**, 356.

[40] A. Stock, *Z. angew. Chem.*, 1926, **39**, 461; A. Schmidt, *ibid.*, p. 786; G. Pinkus, *ibid.*, p. 787; H. Reihlen, *ibid.*, p. 788; F. Gradenwitz, *ibid.*, p. 788; L. Wolff, *ibid.*, p. 789; A. Stock, *ibid.*, p. 790; K. Hofer, *ibid.*, p. 1123; **A.**, 707, 815, 1223.

In heating mercury in a sealed silica bomb, a marked distinction between the liquid and vapour phases was observed immediately before the bomb burst above 1000°; hence the critical temperature of mercury certainly lies above that temperature.[41]

By using the metal as the liquid in a V-shaped silica manometer tube, closed at one end by a sealed-in thermocouple sheath and open at the other end to a measured applied pressure of nitrogen, measurements have been made of the vapour pressures of mercury from 200° (14 mm.) to 397·5° (1490 mm.), of cadmium from 500° (14 mm.) to 836° (1535 mm.), and of zinc from 625° (16 mm.) to 982° (1517 mm.).[42]

Group III.

Some interesting additions have been made to our knowledge of the boron hydrides. Pure diborane has $d^{-112°}$ 0·447 (liquid), $d^{-183°}$ 0·577 (solid), and slowly decomposes at the ordinary temperature, yielding pentaboron hydride, B_5H_{11}, b. p. 0°/57 mm., m. p. about −129°. Unlike the higher hydrides, diborane is not oxidised by air or oxygen at 15°: it is hydrolysed by excess of water to boric acid and hydrogen. Ammonia with B_5H_{11} yields hydrogen and a compound, $B_5H_9(NH_3)_4$, which closely resembles that formed from B_5H_9.[43] This ammine when heated gives a compound, $B_3N_3H_6$. Diborane and ammonia at 15° give an additive compound, $B_2H_6,(NH_3)_2$, which in solution behaves as an alkaline solution of diborane, when heated in a sealed tube gives $B_3N_3H_6$, and reacts with hydrogen chloride according to the scheme: $B_2H_6(NH_3)_2 + 2HCl = B_2H_4Cl_2(NH_3)_2 + 2H_2$. The action of ammonia on diborane at about 200° leads to the replacement of the hydrogen atoms by amino- or imino-groups, so that when excess of ammonia is used, the ultimate product is boroimide, $B_2(NH)_3$. If the ammine, $B_2H_6(NH_3)_2$, is similarly heated, an analogous action occurs, but the amount of ammonia available is insufficient for complete replacement of the hydrogen atoms, and the main and only volatile product is the *compound* $B_3N_3H_6$, mixed with non-volatile condensed substances of composition between $(BNH_2)_x$ and $(BNH)_x$. The compound $B_3N_3H_6$ has b. p. 0°/84·8 mm., m. p. −58·0°, d^{-65} 1·00 (solid), $d^{-57°}$ 0·898 (liquid), $d^{0°}$ 0·824 (liquid), and is unusually stable. At a high temperature, it decomposes into the compound $(BNH)_x$ and hydrogen. It is indifferent to oxygen. In cold water, it dissolves to an initially neutral solution, which gradually becomes alkaline; warm water causes quantitative hydrolysis to boric acid,

[41] L. A. Sayce and H. V. A. Briscoe, *J.*, 1926, 957.
[42] C. H. M. Jenkins, *Proc. Roy. Soc.*, 1926, [*A*], **110**, 456; **A.**, 233.
[43] *Ann. Reports*, 1924, **21**, 37; compare *ibid.*, 1923, **20**, 38.

ammonia, and hydrogen. Ice-cold water yields the *hydrate*, $B_3N_3H_6(H_2O)_3$, which is converted by anhydrous hydrogen chloride into the *compound*, $B_3N_3H_3Cl_3(H_2O)_3$, and hydrogen. The substance $B_3N_3H_6$ and hydrogen chloride slowly yield the non-volatile *compound*, $B_3N_3H_6(HCl)_3$. Ammonia is absorbed by the compound $B_3N_3H_6$, but the reaction appears complex. The behaviour of the compound is best expressed by the constitution $BH<^{NH\cdot BH}_{NH\cdot BH}>NH$.

The action of iodine on diborane affords mainly boron tri-iodide, m. p. 48·1°, and oily products. Diborane is readily converted by hydrogen iodide in the absence of a catalyst at 50° into the unstable *iodo*-derivative, B_2H_5I, m. p. −110°, b. p. 0°/78 mm., $d^{-112°}$ 2·0 (solid), $d^{-108°}$ 1·8 (liquid). Even at low temperatures it decomposes moderately rapidly into diborane and boron tri-iodide. It is rapidly and quantitatively hydrolysed by water to boric acid, hydrogen iodide, and hydrogen. It is converted by sodium amalgam at −35° into the hydride, B_4H_{10}, for which the constitution $BH_3\cdot BH_2\cdot BH_2\cdot BH_3$ is rendered probable if the " ethane " structure for diborane be accepted. A study of the infra-red absorption spectrum of diborane and its *X*-ray analysis affords strong evidence for the constitution $BH_3\cdot BH_3$, and the following structures are inferred for the other hydrides : $B_5H_9 = BH_3\cdot[BH]_3\cdot BH_3$; $B_5H_{11} = BH_3\cdot BH_2\cdot BH\cdot BH_2\cdot BH_3$; $B_6H_{10} = BH_3\cdot[BH]_4\cdot BH_3$; $B_{10}H_{14} = BH_3\cdot[BH]_8\cdot BH_3$.

A modified nomenclature for the boron hydrides is suggested, according to which the term borane is restricted to the " limit hydrides " containing tervalent boron, *e. g.*, B_2H_4 = diborane, B_3H_5 = triborane, $B_{10}H_{12}$ = decaborane. The hydrides richer in hydrogen (the only hydrides already isolated) are termed " hydroboranes," thus, B_2H_6, dihydrodiborane; B_5H_9, dihydropentaborane; B_5H_{11}, tetrahydropentaborane.[44]

Boron sulphide is prepared by heating boric oxide with aluminium sulphide in a current of nitrogen at 1200—1300° : silicon disulphide (m. p. 1090°, *d* 2·02) is similarly obtained when sand is substituted for boric oxide and is separable from accompanying silicon monosulphide by reason of its different volatility.[45]

The freezing-point diagram of the system boron trifluoride–hydrogen sulphide shows two eutectics at −148° and −140°, with 22% and 53% of hydrogen sulphide, respectively, between which lies a maximum at −137° indicating the existence of a compound BF_3,H_2S which is apparently much dissociated at its melting point

[44] A. Stock and E. Pohland, *Ber.*, 1926, **59**, [*B*], 2210, 2215, 2223; A. Stock, *ibid.*, p. 2226; **A.**, 1217, 1218.

[45] E. Tiede and M. Thimann, *ibid.*, p. 1703; **A.**, 1112.

and should therefore not hinder the separation of the constituents by fractional distillation.[46]

By rapid manipulation and exact adherence to specified conditions, aluminium hydroxide is obtained in three forms, α, β, and γ, which behave as distinct chemical compounds, all of the formula $Al(OH)_3$. By heating any one of these in a sealed tube at 250° with 10% ammonia, aluminium metahydroxide, AlO·OH, is obtained, having neither basic nor acidic properties but showing remarkable ability to adsorb enzymes selectively.[47]

Several fluoroaluminates have been prepared and all these can be represented, in conformity with other known aluminium compounds, with a co-ordination number of 6, if in certain cases the nucleus is doubled, *e. g.*, $\left[F_4Al\begin{smallmatrix}F\\<\\F\end{smallmatrix}>AlF_4\right](N_2H_4)_2$. A similar mode of formulation is applicable to a new potassium aluminium fluoride, $AlF_3,2KF,2H_2O$, and also to a number of complex organic fluorides of iron and chromium.[48]

Thallium metasilicate, Tl_2SiO_3, is obtained as a white, amorphous precipitate when a 4% solution of sodium metasilicate is slowly added to a solution containing 2% of thallous nitrate and 4% of thallous hydroxide. An excess of thallous hydroxide must always be present, as the silicate readily undergoes hydrolysis. Thallium orthosilicate, Tl_4SiO_4, is prepared (i) by adding a concentrated solution of sodium metasilicate to a boiling 16·5% solution of thallous hydroxide, a crystalline, canary-yellow precipitate being obtained, which consists of the orthosilicate together with a little metasilicate; (ii) by boiling thallium metasilicate with an excess of 0·75*N*-thallous hydroxide solution; (iii) by shaking finely-divided, precipitated silica with an excess of thallous hydroxide solution. Both the above thallium silicates are anhydrous, in contradistinction to the metasilicates of sodium and lithium, which contain 9 mols. and 1 mol. of water, respectively.[49]

Cerium, lanthanum, praseodymium, neodymium, and samarium have been prepared as chemically pure metals by electrolysis of the fused chlorides in graphite cells, using graphite anodes.[50]

[46] A. F. O. Germann and H. S. Booth, *J. Physical Chem.*, 1926, **30**, 369; **A.**, 475.

[47] R. Willstätter, H. Kraut, and O. Erbacher, *Ber.*, 1925, **58**, [*B*], 2448, 2458; **A.**, 1926, 34, 35.

[48] R. Weinland, I. Lang, and H. Fikentscher, *Z. anorg. Chem.*, 1925, **150**, 47; **A.**, 1926, 136.

[49] K. A. Vesterberg and C. U. Willers, *Arkiv Kemi, Min., Geol.*, 1926, **9**, No. 26, 1; **A.**, 695.

[50] E. E. Schumacher and J. E. Harris, *J. Amer. Chem. Soc.*, 1926, **48**, 3108; see also, for the similar preparation of yttrium, A. P. Thompson, W. B. Holton, and H. C. Kremers, *Trans. Amer. Electrochem., Soc.*, 1926, **49**, 161; **A.**, 489.

Further work has confirmed the individuality of the black oxide of praseodymium, Pr_6O_{11}, which has $d^{20°}$ 6·61, and is not dissociated up to 900° : it is regarded as a salt-like compound of Pr_2O_3 with a higher oxide.[51]

Persistence in the search for element 61 has been rewarded by success. Examination of the *L*-series *X*-ray lines of carefully purified samples of rare earths showed a single faint line in the correct position for L_α 61.[52] Fractional crystallisation of the cerium earths as the magnesium double nitrates concentrates element 61 between neodymium and samarium, both having broad absorption bands capable of masking any bands due to element 61, and fails to give a sufficient concentration of this element for certain detection by the *X*-ray spectrum. If, however, these earths be fractionated as the bromates, element 61 is separated from neodymium and samarium by terbium and gadolinium, respectively. Terbium has but one absorption band and gadolinium has none; hence it became possible to observe faint bands at 6700 and 5905 Å. and stronger bands at 5830, 5816, and 4520 Å. attributed to the new element. The *X*-ray emission spectra of the samples showing these bands gave lines corresponding closely with the calculated positions for L_{α_1}, and L_{β_1}, of element 61; the authors therefore claim to have discovered this element and propose for it the name "illinium."[53]

Group IV.

Pure carbon tetrafluoride has been isolated by liquefying and fractionating the gases evolved at a carbon anode used in the electrolysis of fused beryllium fluoride; it differs from the compounds previously described as carbon tetrafluoride, which were probably mixtures. It has b. p. −150°, $d^{0°}$ 3·034 (air = 1), *M* 87·4, is decomposed by sodium at 500°, by calcium at 600°, and undergoes partial dissociation at 1100°.[54]

Further work on the melting point of graphite, with an improved apparatus in which higher pressures of argon and a closer approximation to "black-body" radiation could be obtained, has given the m. p. 3845° ± 45° Abs., and shown that there is no systematic variation of m. p. over the pressure range 2—9 atm.[55]

[51] W. Prandtl and K. Huttner, *Z. anorg. Chem.*, 1925, **149**, 235; **A.**, 1926, 137; compare *Ann. Reports*, 1924, **21**, 40.

[52] C. J. Lapp, R. A. Rogers, and B. S. Hopkins, *Physical Rev.*, 1925, [ii], **25**, 106; **A.**, 1926, 1083; compare *Ann. Reports*, 1924, **21**, 39.

[53] J. A. Harris and B. S. Hopkins, *J. Amer. Chem. Soc.*, 1926, **48**, 1585; **A.**, 810; J. A. Harris, L. F. Yntema, and B. S. Hopkins, *ibid.*, p. 1594; **A.**, 780; compare L. Rolla and L. Fernandes, *Gazzetta*, 1926, **56**, 435; **A.**, 1083; B. Brauner, *Nature*, 1926, **118**, 84; **A.**, 780.

[54] P. Lebeau and A. Damiens, *Compt. rend.*, 1926, **182**, 1340; **A.**, 710.

[55] E. Ryschkewitsch and F. Merck, *Z. Elektrochem.*, 1926, **32**, 42; **A.**, 232; compare H. Herbst, *Physikal. Z.*, 1926, **27**, 366; **A.**, 670.

In the presence of finely-divided palladium and absence of air, carbon monoxide is oxidised by water to carbon dioxide, with simultaneous production of palladium hydride. Owing to the isolation, in previous work, of small amounts of barium formate, it has been assumed that the primary action consisted in the addition of water to carbon monoxide, with formation of formic acid, which is subsequently decomposed into carbon dioxide and hydrogen. The experimental conditions have therefore been arranged in such a manner as to remove formic acid, if produced by hydration of carbon monoxide, from the dehydrogenating action of palladium, using for this reason alkaline solutions containing a sufficient amount of ethyl alcohol; the presence of alcohol or sodium hydroxide has no influence on the "oxygen-free combustion," of carbon monoxide. Under these conditions, carbonate is immediately formed in the solution, and therefore must be produced directly from carbon monoxide; its production is accompanied by an increase in the hydrogen content of the palladium. Sodium formate, added before the experiment, is found unchanged in amount at its conclusion. The production of carbonate is invariably less, and that of hydrogen greater, than corresponds with the volume of carbon monoxide absorbed. This is caused by the very slow action of palladium on ethyl alcohol, from which hydrogen is withdrawn, with production of acetaldehyde, which, however, never leads to that of recognisable amounts of carbon dioxide.[56]

The energy of the spark discharge necessary to ignite mixtures of carbon monoxide (2 vols.) and oxygen (1 vol.) varies with the moisture content of the gases; for gases saturated at 17° and containing 2% of water the energy is $4{\cdot}6 \times 10^{-3}$ joule; for gases saturated at 0°, containing 0·6% of water vapour (by vol.) it is $29{\cdot}0 \times 10^{-3}$ joule; when the gases are dried over calcium chloride and contain 0·03% of water, it is 126×10^{-3} joule; whilst after drying the gases for 6 months over phosphorus pentoxide, the minimum energy required for ignition is about 0·3 joule. When the gases are dry, the explosion is softer and at atmospheric pressure the reaction is incomplete, its extent depending partly upon the energy of the discharge. At higher pressures, the gases are more readily ignited and the action proceeds further, so that above 10 atm. ignition is instantaneous and the reaction is complete. Spectrograms of explosion flames in dry mixtures at 25 atm. show a complete absence of the steam lines characteristic of the ordinary combustion of carbon monoxide.[57]

[56] W. Traube and W. Lange (and, in part, R. Stahn, R. Justh, and P. Baumgarten), *Ber.*, 1925, **58**, [*B*], 2773; **A.**, 1926, 257; compare *Ann. Reports*, 1912, **9**, 44.

[57] W. A. Bone and F. R. Weston, *Proc. Roy. Soc.*, 1926, [*A*], **110**, 615; **A.**, 480; W. A. Bone, R. P. Fraser, and D. M. Newitt, *ibid.*, p. 634; **A.**, 480.

It has been found that in the chlorination of ferro-silicon the yield of silicon hexachloride may be increased somewhat by adding silicon tetrachloride to the chlorine; this is, of course, in accordance with Martin's conclusions as to the mechanism of this chlorination.[58] By gradually adding to liquid ammonia a solution of disilicon hexachloride in anhydrous ether, ammonium chloride and diaminodiiminodisilane, $NH_2{\cdot}Si(:NH){\cdot}Si(:NH){\cdot}NH_2$, are formed. At −10°, this compound loses ammonia to form polymeric tri-iminodisilane, $\begin{matrix}Si(:NH)\\ |\\ Si(:NH)\end{matrix}\!\!>\!NH$, which is stable at the ordinary temperature but decomposes above 400° with some formation of silicocyanogen, Si_2N_2. These compounds are extremely sensitive to oxygen and moisture. From the products of the action of magnesium phenyl bromide on disilicon hexachloride, dichlorodiphenylmonosilane, $SiPh_2Cl_2$, b. p. 166°/17 mm., has been isolated.[59]

In the course of further experiments upon silicic acids, the curious observation has been made that a certain form of silicic acid is volatile in steam.[60]

Pure germanochloroform has been prepared by the action of hydrogen chloride on germanium dichloride; it has m. p. −71°, b. p. 75·2°, d^0 1·93, and the vapour pressure has been measured over the range −25° to 78·3°. Decomposition of the compound begins at 140° and is rapid at 170°, at first by dissociation to yield $GeCl_2 + HCl$, later to give the tetrachloride and metallic germanium. It is oxidised, even at 0°, by oxygen, probably according to the scheme: $4GeHCl_3 + O_2 = 2GeCl_4 + 2GeCl_2 + 2H_2O$.[61] Germanium tetrachloride when pure, or in ethereal solution, reacts with dry ammonia to give hexamminogermanic chloride, $[Ge,6NH_3]Cl_4$, as a white powder which has no appreciable ammonia pressure at the ordinary temperature and may be kept for some days over concentrated sulphuric acid without loss of weight. In aqueous solution or in moist air it is slowly hydrolysed forming germanic hydroxide. When the solid is treated at 0° with ammonia at 3 atm., it forms a second ammine, $GeCl_4{,}16NH_3$, as a colourless liquid having an ammonia pressure of 760 mm. at −4°. Compounds analogous to the hexammine have been obtained with mono-, di-, and tri-ethylamines, propylamine, and butylamine.[62]

Tertiary stannous phosphate, $Sn_3(PO_4)_2$, is a white, amorphous

[58] J. B. Quig and J. A. Wilkinson, *J. Amer. Chem. Soc.*, 1926, **48**, 902; **A.**, 589; compare G. Martin, *J.*, 1914, **105**, 2836.

[59] R. Schwarz and W. Sexauer, *Ber.*, 1926, **59**, [*B*], 333; **A.**, 369.

[60] R. Willstätter, H. Kraub, and K. Lobinger, *ibid.*, 1925, **58**, [*B*], 2462; **A.**, 1926, 36.

[61] L. M. Dennis, W. R. Orndorff, and D. L. Tabern, *J. Physical Chem.*, 1926, **30**, 1049; **A.**, 924.

[62] W. Pugh and J. S. Thomas, *J.*, 1926, 1051; **A.**, 695.

powder, $d_{4°}^{17·4°}$ 3·823, insoluble in water, but soluble in mineral acids and alkali hydroxides; it is produced by adding a 10% solution of disodium hydrogen phosphate to a cold 10% solution of stannous sulphate containing a little sulphuric acid. Stannous hydrogen phosphate, $SnHPO_4$, crystallises in colourless tablets, $d_{4°}^{15·5°}$ 3·476, from the solution obtained by dissolving granulated tin in phosphoric acid (*d* 1·23), or in small, silky crystals on adding water to a solution obtained by dissolving tin in phosphoric acid (*d* 1·7). Stannous dihydrogen phosphate, $Sn(H_2PO_4)_2$, results on heating the previous salt with phosphoric acid at 140° and cooling the solution over phosphoric oxide; it crystallises in the form of highly refractive rhombs, $d_{4°}^{22·8°}$ 3·167, which are readily decomposed by water. Stannous pyrophosphate, $Sn_2P_2O_7$, is obtained as a white powder, $d_{4°}^{16·4°}$ 4·009, when the monohydrogen phosphate is heated at 350—400° in a current of carbon dioxide. Stannous metaphosphate, $Sn(PO_3)_2$, is a white, glassy mass, $d_{4°}^{22·8°}$ 3·38, formed by heating the dihydrogen phosphate at 390° in a current of carbon dioxide. The stannous phosphates are more readily hydrolysed than the corresponding lead compounds, but otherwise are relatively stable.[63]

Pure zirconium metal has been obtained by preparing the pure tetraiodide, resubliming it in a closed apparatus, and volatilising it at 600° in a vessel containing a fine tungsten wire heated electrically to 1800°. Under these conditions, the iodide dissociates and pure zirconium is deposited as a rod, of which the tungsten wire forms only 0·01% by volume. It has m. p. 2200° Abs., *d* 6·5, is comparable with copper in ductility, and retains its lustre in air at the ordinary temperature but is superficially oxidised at high temperatures.[64]

A new method of separating hafnium from zirconium makes use of the fact that freshly-precipitated zirconium phosphate is soluble in oxalic acid and, on adding hydrochloric or sulphuric acid, is reprecipitated in a form which is readily filtered and affords a comparatively rapid separation of the hafnium in the precipitates. 100 Kg. of a preparation containing 47·5% of zirconium and less than 0·5% of hafnium were treated, and after 26 fractionations hafnium containing not more than 1% of zirconium was obtained. The hafnium content of each fraction was determined with an *X*-ray spectrograph and confirmed chemically at intervals. This method of separation has the advantages over fractional crystallisation of the double fluorides that it is more rapid, and that the hafnium

[63] K. Jabłczyński and W. Więckovski, *Z. anorg. Chem.*, 1926, **152**, 207; **A.**, 588.

[64] J. H. de Boer and J. D. Fast, *ibid.*, **153**, 1; **A.**, 699.

accumulates in the less instead of in the more soluble fraction. From the pure hafnium phosphate, the metal (*d* 12·1) was prepared *via* the hydroxide, oxide, chloride, metal, iodide, metal.[65]

Some most interesting work is reported by Smits. A quartz apparatus, resembling a mercury-arc lamp but heated externally by gas-burners, was filled with molten lead of the highest purity and run as a lead-arc lamp, in which, by rocking the tube, the arc was made and broken several times per second. At first, the lamp showed the lead spectrum only, but after running at 80 volts and 40 amp. for 10 hours, the spectrum of the light emitted showed strong lines of mercury and thallium, and in experiments in which sparking was employed to obtain high current densities, spectra showing all the principal lines of mercury were obtained. In other experiments, a heavy spark-discharge between lead electrodes immersed in carbon disulphide produced a fine deposit of dispersed lead. This lead was collected and heated in air and the distillate, when treated with iodine vapour, gave visible traces of mercuric iodide; the same test applied to the lead electrode material gave negative results.

The earlier experiments with the quartz–lead lamp were necessarily of short duration, as the tubes were so blackened by a film of lead silicate and silicon that observation became impossible after a few hours. A modified design of lamp now employed permits much longer runs and the light after 39 hours shows a very strong mercury spectrum. In yet another experiment, 850 g. of lead removed from a lamp after being used to produce an intermittent arc for 188 hours were heated to 800° in a quartz apparatus in a current of pure nitrogen, which then passed through two U-tubes cooled in liquid air where 5 mg. of mercury condensed. Precisely similar treatment of the same quantity of the same sample of original lead which had not been used in a lamp gave no trace of mercury. These results are interpreted to indicate that a transmutation of lead into thallium and mercury has occurred, and whilst, of course, their general acceptance must await independent confirmation, the experiments here referred to do seem to afford strong evidence of transmutation.[66]

Group V.

The heat of formation of active nitrogen has been determined by causing a current of activated gas to react with nitric oxide in a calorimeter and measuring the heat evolved and the amount of

[65] J. H. de Boer, *Z. anorg. Chem.*, 1926, **150**, 210; **A.**, 373.

[66] A. Smits and A. Karssen, *Z. Elektrochem.*, 1926, **32**, 578; A. Smits, *Nature*, 1926, **117**, 13; **A.**, 106; compare *idem*, *Z. anorg. Chem.*, 1926, **155**, 269; **A.**, 1015; (Miss) A. C. Davies and F. Horton, *Nature*, 1926, **117**, 152; **A.**, 221; A. Smits, *ibid.*, p. 620; **A.**, 554.

nitrogen peroxide produced. The mean value obtained for the heat of formation, 42,500 cal./g.-mol. (about 2·0 volts), supports the hypothesis that active nitrogen is nitrogen in a metastable molecular form. Observations of the effect of various gases in extinguishing the fluorescence of active nitrogen indicate that only those for which the critical increments are less than a value approximately equal to the above heat of formation have a positive effect.[67] On the other hand, the second positive group of bands, which predominates in the discharge on activation of nitrogen, is believed to be due to the atom.[68]

Nitrous oxide has been synthesised by passing an electric discharge through nitrogen at a low pressure contained in a tube of fused silica, the walls of which had previously been saturated with oxygen by passing a discharge through the tube filled with that gas. The nitrous oxide was isolated as it was formed by condensing it in a U-tube surrounded with liquid air.[69]

In the course of measurements of its compressibility up to 160 atm. and over the temperature range −80° to 10°, it has been observed that under prolonged compression nitric oxide decomposes, yielding a blue, liquid mixture of nitrous oxide and nitrous anhydride. At 700 atm. the decomposition is very rapid. Freshly-prepared and liquefied nitric oxide is but faintly blue in colour, and the pure substance would probably be colourless, but multiple liquefaction does not effect purification, since the intensity of the blue colour is thereby gradually increased.[70] On the other hand, nitric oxide is formed in appreciable amounts (up to 25% of that required by the equation $2N_2O \longrightarrow 2NO + N_2$) by dissociation of nitrous oxide at 1300°. At lower temperatures (700°), the decomposition is slower and proceeds chiefly according to the exothermic reaction, $2N_2O \longrightarrow 2N_2 + O_2$; the former, slightly endothermic, reaction is favoured by rise of temperature.[71]

It has been found that the decomposition of nitrogen pentoxide is not accelerated by infra-red radiation corresponding with its strong absorption bands; this is contrary to the predictions of the radiation theory.[72] A study of the thermal decomposition of nitrogen pent-

[67] E. J. B. Willey and E. K. Rideal, *J.*, 1926, 1804; **A.**, 893; E. J. B. Willey, *Nature*, 1926, **117**, 381; **A.**, 336; *ibid.*, **118**, 735; **A.**, 1213.

[68] M. Duffieux, *ibid.*, **117**, 302; **A.**, 336; compare (Lord) Rayleigh, *ibid.*, p. 381; **A.**, 336.

[69] D. L. Chapman, R. A. Goodman, and R. T. Shepherd, *J.*, 1926, 1404; **A.**, 811.

[70] E. Briner, H. Biedermann, and A. Rothen, *Helv. Chim. Acta*, 1925, **8**, 923; **A.**, 1926, 16.

[71] E. Briner, C. Meiner, and A. Rothen, *ibid.*, 1926, **9**, 409; **A.**, 685.

[72] H. A. Taylor, *J. Amer. Chem. Soc.*, 1926, **48**, 577; **A.**, 485; compare F. Daniels, *ibid.*, p. 607; **A.**, 485.

oxide at low pressures has shown that dissociation is not retarded by lowering of pressure, but below a critical pressure, approximately 0·25 mm., it is gradually accelerated with falling pressure until, at the lowest pressures, the rate of dissociation becomes approximately constant at about five times the normal value. This curious observation is quite irreconcilable with all "chain" mechanisms, and is most readily interpreted on the assumption that a definite fraction of the activated molecules always undergoes decomposition irrespective of pressure, but that a larger fraction (about four-fifths) does not decompose if it collides within 10^{-6} sec. after activation, but is deactivated by collision. Calculations on this basis are in good agreement with experiment. A possible explanation of the two different types of activated molecules is offered, based on the fact that there are four N–O linkings, and only one shared N–O linking in the molecule of the pentoxide. Activation of one linking causes decomposition—activation of the shared linking invariably so; activation of the others, only after a time interval and if collisions do not intervene.[73]

A number of reactions of elements electronegative to nickel upon ammonio-bases in liquid ammonia solution have been investigated: the initial reaction is of the type $Cl_2 + 2KOH \longrightarrow KCl + KClO + H_2O$. By the action of sodamide or potassamide upon excess of tin amalgam, new *sodium* and *potassium ammoniostannites*, Na (or K)[$Sn(NH_2)_3$], have been obtained.[74] A break at 310° in the decomposition curve of the compound $PCl_5,10NH_3$ corresponds with a break observed at the same temperature with a mixture of ammonium chloride and sand, and thus suggests that the substance is partly a mixture of ammonium chloride and the amine $P(NH_2)_5$—a view which is supported by the action of liquid ammonia on the substance.[75]

Pyridine hydrazinedisulphonate is prepared in 80—85% yield by the action of chlorosulphonic acid on a suspension of hydrazine sulphate in cold pyridine and subsequent precipitation of the salt by addition of ethyl alcohol; the corresponding ammonium ($+ H_2O$) and sodium ($+ 2H_2O$) salts are described. The pyridine salt is oxidised by sodium hypochlorite in the presence of water at −20° to the azo-compound, isolated by addition of potassium chloride as potassium azodisulphonate, $SO_3K{\cdot}N{:}N{\cdot}SO_3K$.[76]

Red or yellow phosphorus reacts with water at 238—360° and

[73] H. S. Hirst and E. K. Rideal, *Proc. Roy. Soc.*, 1925, [*A*], **109**, 526; **A.**, 1926, 32.

[74] F. W. Bergstrom, *J. Physical Chem.*, 1926, **30**, 12; **A.**, 254.

[75] H. Perpérot, *Bull. Soc. chim.*, 1925, [iv], **37**, 1540; **A.**, 1926, 137.

[76] E. Konrad and L. Pellens, *Ber.*, 1926, **59**, [*B*], 135; **A.**, 370.

57—360 atm. to form phosphine and orthophosphoric acid thus: $4P_2 + 12H_2O \longrightarrow 3H_3PO_4 + 5PH_3$. If hydrogen be added, the proportion of phosphine increases until, with dry hydrogen at 360° or less, it is the sole product. When phosphorus is heated with water for a short time at 248° and 48 atm. and the reaction is rapidly interrupted, there is formed a crystalline purple phosphorus, *d* 1·93, which has an ignition temperature 210°. At higher temperatures, and pressures (360—380° and >90 atm.) crystalline black phosphorus, *d* 3·06, is formed, apparently by decomposition of phosphine first formed.[77]

The velocity of air-blast required to remove the glow from phosphorus and maintain it downstream may be used as a measure of the rate of propagation of the glow. Using this method in an extension of Rayleigh's experiments, it has been found that inhibitors, such as ethylene, benzene, chloroform, and aniline, diminish the rate of propagation, and to an extent which is lessened by rise of temperature, and thus act in this matter just as oxygen does.[78]

The addition of stannic chloride, either as solid or in very concentrated solution, to a concentrated solution of sodium hypophosphite produces a voluminous, white precipitate of a strongly reducing substance, the analysis of which corresponds with the formula $SnCl_4,Sn(H_2PO_2)_4,3H_2O$. When heated, the substance is dehydrated at 140°, and decomposes at 190° with a characteristic reddening and the evolution of phosphine. If the heating is stopped immediately the red colour appears, and the mass extracted with concentrated hydrochloric acid, a bright red residue remains, which has very strong reducing properties and a composition approximating closely to that of phosphorus suboxide, P_4O.[79]

A large number of new complex metallic phosphites and pyrophosphates have been prepared.[80]

Phosphorus nitride, PN, has been obtained by passing a discharge between aluminium electrodes in nitrogen at about 200 mm. in a tube lined with yellow phosphorus, extracting the product with carbon disulphide, and heating the residue in porcelain at 550° in a stream of nitrogen at 12 mm. pressure. The residual nitride is a voluminous, yellowish-brown powder, very resistant to chemical agents.[81]

The preparation of an acid barium vanadate, $2BaO,3V_2O_5,12H_2O$,

[77] V. Ipatiev and W. Nikolajev, *Ber.*, 1926, **59**, [*B*], 595; **A.**, 487.

[78] H. J. Emeléus, *J.*, 1926, 1336; **A.**, 777.

[79] A. Terni and C. Padovani, *Atti R. Accad. Lincei*, 1925, [vi], **2**, 501; **A.**, 1926, 255.

[80] A. Rosenheim, S. Frommer, H. Gläser, and W. Händler, *Z. anorg. Chem.*, 1926, **153**, 126; **A.**, 696.

[81] W. Moldenhauer and H. Dörsam, *Ber.*, 1926, **59**, [*B*], 926; **A.**, 696.

has been described; and from this salt, by interaction with metallic salts, similar vanadates of nickel, cobalt, copper, beryllium, cadmium, and manganese are obtained. They take up gaseous ammonia slowly, and combine more rapidly with liquid ammonia, to form hexammines.[82]

Group VI.

Excess of hydrogen sulphide acts upon 1% aqueous potassium permanganate according to the scheme $10KMnO_4 + 22H_2S \longrightarrow 3K_2SO_4 + 10MnS + 2K_2S_2O_3 + 22H_2O + 5S$; in the earlier stages of the reaction some dithionate is formed.[83] Experiments upon the decomposition of dilute aqueous thiosulphuric acid have shown that the yellow colour characteristic of such solutions is due to a sulphur compound derived from the oxide S_2O_3; about 40% of the total sulphur present exists in this form.[84] In confirmation of this, it is found that anhydrous thiosulphates with liquid sulphur dioxide at low temperatures yield yellow solid compounds, $K_2S_2O_3,SO_2$ and $Rb_2S_2O_3,SO_2$, which give clear yellow aqueous solutions in which the equilibrium $S_2O_3'' + SO_2 \rightleftharpoons [S_2O_3(SO_2)]''$ exists.[85]

The method of intensive drying has been applied to a further study of the complexity of the solid state; repeated distillation of the dried ice-like form of sulphur trioxide yields the high-melting (as distinct from the low-melting) asbestos-like form, and this gives marked evidence of complexity by a great decrease of vapour pressure (from 591 to 37 mm.) on distillation. This low vapour pressure is substantially constant at 18°, but at higher temperatures it increases, approaching asymptotically the value corresponding to inner equilibrium. The establishment of equilibrium is hastened by incidence of *X*-rays, and all forms yield identical *X*-ray photographs. The original papers should be consulted for a full account of the experimental method and of the argument directed to establish the great complexity of the system formed by this simple compound.[86]

It is convenient here to mention other work of a kindred nature. To determine whether intensive drying results in a fixing of the inner equilibrium, or a displacement of the inner equilibrium followed by fixation, measurements of the vapour pressure of intensively dried nitrogen tetroxide and *n*-hexane have been made. Nitrogen tetroxide, after intensive drying for 23 months at the

[82] F. Ephraim and G. Beck, *Helv. Chim. Acta*, 1926, **9**, 38; **A.**, 370.

[83] H. B. Dunnicliff and S. D. Nijhawan, *J.*, 1926, 1; **A.**, 256.

[84] E. H. Riesenfeld and E. Grünthal, *Medd. K. Vetenskapsakad. Nobel-Inst.*, 1925, **6**, No. 9, 1; **A.**, 1926, 257.

[85] F. Foerster and R. Vogel, *Z. anorg. Chem.*, 1926, **155**, 161; **A.**, 1016.

[86] A. Smits and P. Schoenmaker, *J.*, 1926, 1108, 1603; **A.**, 669, 785.

ordinary temperature in an apparatus the glass of which was not freed from capillaries, showed an increase in the vapour pressure of 1·9 cm. of mercury; a part of the liquid was then distilled off, and the increase fell to 0·4 cm., but after a further 11 days this had risen to 1·47 cm. In another apparatus made of capillary-free glass, a much more rapid drying effect was obtained, for after 16 months the vapour pressure had risen by 3·3 cm. On raising the temperature, the increase passed through a maximum, as had been anticipated on theoretical grounds. The changes of vapour pressure, and of colour to a deeper brownish-red, prove that the drying process had effected a displacement of the inner equilibrium in the direction $N_2O_4 \longrightarrow 2NO_2$.

With *n*-hexane, intensive drying at about 40° results in a decrease of vapour pressure. After only 14 weeks, this reached 0·9 cm., showing that, in contrast to nitrogen tetroxide, the inner equilibrium is here shifted towards the less volatile component. The decrease was augmented by raising the temperature, and after distilling off a portion of the liquid at the drying temperature, the vapour pressure tended to revert to its previous value, showing that the inner equilibrium had not been reached.[87]

Pyrosulphuryl chloride has been prepared by the action of carbon tetrachloride on sulphuric or chlorosulphonic acid at 80°, and is a hygroscopic substance, $d^{19°}$ 1·834, $n_D^{19°}$ 1·449, b. p. 57°/30 mm., 52°/15 mm., having a characteristic odour. When heated, it dissociates irreversibly according to the schemes $S_2O_5Cl_2 \longrightarrow SO_3 + SO_2 + Cl_2$ and $S_2O_5Cl_2 \longrightarrow SO_3 + SO_2Cl_2$. Measurements of its diamagnetism and molecular refraction indicate the constitution: S(:O)(OCl)·O·S(:O)(OCl).[88]

When chromium trioxide is heated at 265°, oxygen is evolved and the liquid slowly solidifies to a dark brownish-violet mass of a new oxide Cr_5O_{13}, which, like the known oxide, Cr_5O_{12}, appears to be a chromate of chromium.[89] The chromium carbonyl, $Cr(CO)_6$, has been prepared by slowly adding ethereal magnesium phenyl bromide to an ether–benzene suspension of chromium chloride in presence of carbon monoxide below 10°.[90]

Selenic–uranic acid, $H_2[UO_3(SeO_4)],2H_2O$, diselenic–uranic acid, $H_6[UO_4(SeO_4)_2],2H_2O$ (and with $6H_2O$), and triselenic–diuranic acid,

[87] A. Smits, W. de Liefde, E. Swart, and A. Claassen, *J.*, 1926, 2657; **A.**, 1206; A. Smits, *ibid.*, p. 2655; **A.**, 1205; compare S. B. Mali, *Z. anorg. Chem.*, 1925, **149**, 150; **A.**, 1926, 117; J. W. Williams, *J. Amer. Chem. Soc.*, 1925, **47**, 2644; **A.**, 1926, 15.

[88] V. Grignard and P. Muret, *Compt. rend.*, 1926, **183**, 581; **A.**, 1113; *ibid.*, p. 713; **A.**, 1218.

[89] A. Simon and T. Schmidt, *Z. anorg. Chem.*, 1926, **153**, 191; **A.**, 697.

[90] A. Job and A. Cassal, *Compt. rend.*, 1926, **183**, 392; **A.**, 1017.

$H_6[UO_2(UO_4)(SeO_4)_3],7H_2O$, and a number of potassium and ammonium salts derived therefrom, have been prepared.[91]

By heating the known uranium nitride, U_3N_4, at 1740° and 1900°, two new nitrides, U_5N_4 and U_5N_2, are obtained: these differ from U_3N_4 in being completely soluble in acids with the evolution of hydrogen and conversion of the nitrogen into ammonium salts.[92]

Group VII.

Several oxidising reactions of fluorine have been investigated. Fluorine with aqueous ammonium hydrogen sulphate or dry potassium hydrogen sulphate yields considerable amounts of the persulphates, in the latter case accompanied by potassium fluorosulphonate, $KFSO_3$.[93]

Hydrogen chloride is found to combine readily with certain metallic sulphates, forming compounds of the type $XSO_4,2HCl$; this occurs chiefly in the cases where the metallic chlorides do not readily yield hydrogen chloride when treated with concentrated sulphuric acid, and the temperature at which the evolution of gas begins is approximately the dissociation temperature of the complex.[94] Determinations have been made of the vapour pressure of pure chlorine dioxide from the f. p. −59° to the b. p. +11°.[95]

In an interesting investigation of the influence of water on the union of halogens with hydrogen, it has been observed that whilst the combination of hydrogen and iodine can be inhibited by intensive drying, the decomposition of hydrogen iodide, similarly dried and at the same temperature, proceeds apparently unhindered. Hence, in this case, as in those previously mentioned, intensive drying shifts the position of equilibrium.[96]

Iodic acid and stannic chloride in dilute nitric acid solution yield, according to the conditions, dihydroxytetraiodatostannic acid, $Sn(IO_3)_4(OH)_2H_2$, or stanni-iodic acid, $Sn(IO_3)_6H_2$. The alkali-metal salts of the latter acid and also of tetrahydroxydi-iodatostannic acid, $Sn(IO_3)_2(OH)_4H_2$, have been prepared. Iodic acid and antimony pentachloride yield trihydroxytri-iodatoantimonic acid, $Sb(IO_3)_3(OH)_3H$.[97]

[91] J. Meyer and E. Kasper, *Z. anorg. Chem.*, 1926, **155**, 49; **A.**, 925.

[92] O. Heusler, *ibid.*, **154**, 353; **A.**, 909.

[93] F. Fichter and K. Humpert, *Helv. Chim. Acta*, 1926, **9**, 467, 602, 692; **A.**, 699, 925.

[94] F. Ephraim, *Ber.*, 1925, **58**, [*B*], 2262; **A.**, 1926, 36; *ibid.*, **59**, [*B*], 790; **A.**, 587.

[95] F. E. King and J. R. Partington, *J.*, 1926, 925; **A.**, 569.

[96] B. Lewis and E. K. Rideal, *J. Amer. Chem. Soc.*, 1926, **48**, 2553; **A.**, 1111.

[97] P. Rây and S. N. Ray, *J. Indian Chem. Soc.*, 1926, **3**, 110; **A.**, 1015.

Although a good deal of discussion has taken place upon the supposed discovery of dvi-manganese previously reported, nothing substantial has been added to our knowledge of the element.[98]

Group VIII.

New hydrides of cobalt, iron, and chromium have been obtained by the interaction of the chlorides of those metals with hydrogen in presence of magnesium phenyl bromide. Cobalt hydride has the formula CoH_2; iron dihydride, FeH_2, is a black powder; iron hexahydride, FeH_6, is a black, viscous oil; chromium trihydride, CrH_3, is a black precipitate.[99]

A study of the composition of various ferro- and ferri-cyanides, prepared in a variety of ways, has led to the conclusion that ordinary Prussian blue is the ferrous salt of a complex acid formulated as follows : [1] $\overset{H}{Fe}\!>\!Fe(CN)_6\!-\!Fe\!-\!Fe(\underset{Fe}{CN})_6\!-\!Fe\!-\!Fe(CN)_6\!<\!\overset{(OH)_2}{H}$

The identity of the absorption spectra of ferronitricoxide salts in aqueous solution confirms the view that they all give the same coloured cation, $FeNO^{\cdot}$: and the similarity between these spectra and those of the black series of Roussin's salts lends support to the view that the latter should be formulated [2]

$$\left[\begin{matrix}Fe(NO_2)S\\Fe(NO_2)S\end{matrix}\!>\!Fe\!<\!\begin{matrix}Fe(NO_2)S\\NO\end{matrix}\right]K.$$

A number of interesting papers on complex cobalt salts cannot be summarised in the space available and must be dismissed with a reference.[3]

Platinum tribromide is obtained by heating platinum tetrabromide between 370° and 405°; above 410°, the tribromide loses bromine to form the dibromide, but this is stable over a range of only 5°.

[98] J. Heyrovský, *Nature*, 1926, **117**, 16; **A.**, 138; J. G. F. Druce, *ibid.*, p. 16; **A.**, 138; V. Dolejšek, J. G. F. Druce, and J. Heyrovský, *ibid.*, p. 159; **A.**, 227; V. Dolejšek and J. Heyrovský, *Chem. Listy*, 1926, **20**, 4; **A.**, 258; F. H. Loring, *Chem. News*, 1926, **132**, 101; **A.**, 338; O. Zvjaginstsev, M. Korsunski, and N. Seljakov, *Nature*, 1926, **118**, 262; **A.**, 934; B. Polland, *Compt. rend.*, 1926, **183**, 737; **A.**, 1194; F. H. Loring and J. G. F. Druce, *Chem. News*, 1925, **131**, 337; **A.**, 12.

[99] T. Weichselfelder and B. Thiede, *Annalen*, 1926, **447**, 64; **A.**, 372.

[1] N. Tarugi, *Gazzetta*, 1925, **55**, 951; **A.**, 1926, 259.

[2] W. Manchot and E. Linckh, *Ber.*, 1926, **59**, [*B*], 406, 412; **A.**, 452, 453.

[3] E. H. Riesenfeld (with W. Petrich), *Medd. K. Vetenskapsakad. Nobel-Inst.*, 1925, **6**, No. 6, 1; **A.**, 1926, 259; R. Klement, *Z. anorg. Chem.*, 1926, **150**, 117; **A.**, 372; F. L. Hahn, H. A. Meier, and H. Siegert, *ibid.*, p. 126; **A.**, 372; F. M. Jaeger and P. Koets, *Proc. K. Akad. Wetensch. Amsterdam*, 1926, **29**, 59; **A.**, 697; J. Meyer and K. Gröhler, *Z. anorg. Chem.*, 1926, **155**, 91; **A.**, 925; B. K. Paul and P. V. Sarkar, *Ann. Chim.*, 1926, [x], **5**, 199; **A.**, 588.

Platinum tetraiodide is produced by heating platinum with iodine in a sealed tube at 240—300°, and this is converted to the tri-iodide at 350—400°.[4]

Tensimetric determinations of the molecular weights of *cis*- and *trans*-dichlorodiamminoplatinum in liquid ammonia show that the *cis*-salt has a normal and the *trans*-salt a double molecular weight. The latter salt is therefore formulated :[5]

$$\left[Cl_2(NH_3)_2Pt\begin{matrix}<NH_3\\<NH_3\end{matrix}>PtCl_2\right].$$

The action of hydrogen peroxide or ozone on complex compounds of bivalent platinum renders the platinum quadrivalent and thereby adds two negative groups to it. Thus, from Peyronne's chloride are obtained the dihydroxy-compound, $[Pt,2NH_3,Cl_2(OH)_2]$, and a new hydroxypentamminoplatinic carbonate, $[Pt,5NH_3,OH]_2(CO_3)_3$.[6]

By passing carbon monoxide into a suspension of palladous chloride in anhydrous alcohol at 0°, or by passing the gas, charged with methyl alcohol vapour, over palladous chloride at 15°, the compound $PdCl_2,CO$ is obtained. It readily decomposes into palladium and carbon dioxide.[7]

Ruthenium tetrachloride, $RuCl_4,5H_2O$, has been obtained as hygroscopic, reddish-brown, monoclinic crystals. It is formed when a solution of hydroxytetrachlororuthenic acid in concentrated hydrochloric acid is saturated with chlorine for 5 hours at 100° and then evaporated in a current of dry chlorine. It is hydrolysed in dilute solution, but in a strong solution is stable at 15°, does not liberate iodine from potassium iodide, gives a black precipitate with silver nitrate and forms crystalline double salts with potassium and ammonium chlorides.[8]

Two new chlorides of rhodium, RhCl and $RhCl_2$, result from the action of chlorine on rhodium at 948—968°; and by dissociation of rhodium trioxide at 750° in oxygen, two new oxides, Rh_2O and RhO, insoluble in acids, but readily reducible by hydrogen, have been obtained.[9]

H. V. A. Briscoe.

[4] L. Wöhler and F. Müller, *Z. anorg. Chem.*, 1925, **149**, 377; **A.**, 1926, 259.

[5] H. Reihlen and K. T. Nestle, *Annalen*, 1926, **447**, 211; **A.**, 699.

[6] L. Tschugaev and W. Chlopin (with E. Fritzmann), *Z. anorg. Chem.*, 1926, **151**, 253; **A.**, 373.

[7] W. Manchot and J. König, *Ber.*, 1926, **59**, [*B*], 883; **A.**, 698; compare W. Manchot, *ibid.*, 1925, **58**, [*B*], 2518; **A.**, 1926, 138.

[8] S. Aoyama, *Z. anorg. Chem.*, 1926, **153**, 246; **A.**, 698.

[9] L. Wöhler and W. Müller, *ibid.*, 1925, **149**, 125; **A.**, 1926, 138.

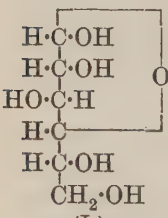
ORGANIC CHEMISTRY.

Part I.—Aliphatic Division.

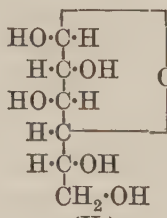
Carbohydrates.

Oxide-Ring Structure in the Sugar Group.

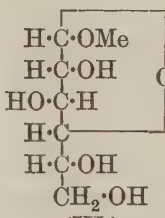
The traditional formulæ for α- and β-glucose (I and II) and for α- and β-methylglucoside (III and IV) have been accepted without serious question and in the absence of rigid proof during several decades. Fischer's choice of a five-membered ring to represent the cyclic system in glucosides and disaccharides established a mode of formulation which has been generally accepted for 40 years. The same cyclic structure has been applied to the free sugars themselves, in view of their existence in two stereochemical forms quite apart from the usual *d*- and *l*-enantiomorphs. E. F. Armstrong [1] first showed the structural relationships of α- and β-glucoses to α- and β-methylglucosides, and this experimental proof carries conviction independently of the precise oxide-ring structure which may be applied to these substances.



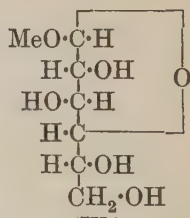
(I.)



(II.)



(III.)



(IV.)

A criticism of the validity of Fischer's statement as to the structural identity of α- and β-methylglucosides was contributed by Nef [2] in 1914. The latter author discovered a second crystalline gluconolactone which he described as a β-lactone, isomeric with the γ-gluconolactone already known. He deduced from this result that the two lactones should correspond with two structurally different types of glucoses or methylglucosides, and as only two such forms were known he advanced the opinion that α- and β-methylglucosides contained different oxide rings, one being a butylene oxide and the other a propylene oxide.

[1] *J.*, 1903, **83**, 1305. [2] *Annalen*, 1914, **403**, 204.

Fischer's reply [3] is noteworthy not merely since it confirmed the essential stereochemical relationships as opposed to the structural isomerism of the glucosides suggested by Nef, but because in the same paper he announced the discovery of a new variety of methyl-glucoside which he designated the γ-form. This was structurally different from either of the previously known forms, and was prepared by condensing glucose with methyl alcohol at a lower temperature. The idea that this new glucoside might be correlated with Nef's second lactone was not developed, but the occasion is interesting historically since the comparative study of derivatives of γ-sugars alongside those of the normal sugars has latterly furnished the initial data for the revision of the structural formulæ which has now been proposed.

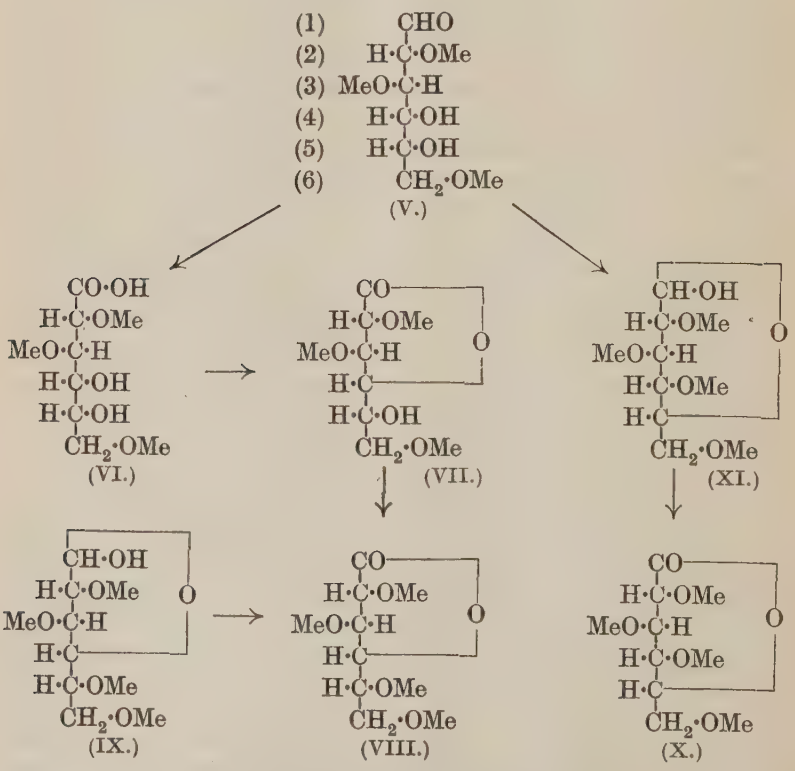
A scrutiny of the evidence for the butylene-oxide formula ascribed to glucose and the normal glucosides reveals little more than an assumed analogy of their ring structure with that of the γ-lactones to which sugars most readily give rise on oxidation. Inasmuch as the " lactol " ring of a sugar is not preserved during oxidation to the lactone, the latter being formed through the intermediate stage of the open-chain acid, the supposed identity of the cyclic forms of lactone and sugar is seen to depend on an assumed similarity of tendency of open chains, whether they be aldoses or polyhydroxy-acids, to undergo the same type of ring closure. Although there are grounds for this expectation as between aldoses and ketoses, yet there is less immediate reason for anticipating the same consistency in type, character, or stability of ring forms as between, say, hexoses and their carboxylic acids.

This problem has been studied [4] from the standpoint of the lactones derived from simple methylated sugars, and in a series of papers a comparison has been made of those lactones obtained from methylated hexoses and pentoses of the normal or usual type with others which were derived from the methylated γ-sugars. The two series of lactones differed widely in their properties, but it was found that sugars giving lactones of one structural type could be so transposed as to give lactones of the second type. A simplified example of this inter-relationship as applied to glucose is as follows : A partly substituted glucose was selected, having substituent methyl groups in the 2 : 3 : 6-positions, and, although this is known to possess an oxide-ring structure, it is preferable at this stage to

[3] *Ber.*, 1914, **47**, 1980.

[4] W. N. Haworth, *Nature*, 1925, **116**, 430; W. Charlton, W. N. Haworth, and S. Peat, *J.*, 1926, 89; **A.**, 273; W. N. Haworth and G. C. Westgarth, *ibid.*, p. 880; **A.**, 600; W. N. Haworth and V. S. Nicholson, *ibid.*, p. 1899; **A.**, 1025.

represent this 2 : 3 : 6-trimethyl glucose provisionally by the aldose formula (V) in order to avoid any anticipation of the issue of the argument. Clearly the oxide ring can only be in either position 1 : 4 or 1 : 5. On oxidation, the sugar (V) gives the 2 : 3 : 6-trimethyl gluconic acid (VI), and this passes easily and almost completely into the lactone (VII) which, on the basis of Hudson's lactone rule,[5] is identified as a γ-lactone, *i.e.*, having the ring in position 1 : 4. Methylation of the exposed hydroxyl group leads to the fully methylated 2 : 3 : 5 : 6-tetramethyl gluconolactone (VIII), which has latterly [6] been obtained as a crystalline solid. This yields the crystalline phenylhydrazide of the corresponding acid. The same lactone is also obtained on oxidising the tetramethyl γ-glucose derived from the methylation of Fischer's γ-methylglucoside, and therefore the structure of tetramethyl γ-glucose is represented by formula (IX), and Fischer's γ-methylglucoside thus contains a butylene-oxide ring.



[5] *J. Amer. Chem. Soc.*, 1910, **32**, 338.

[6] W. N. Haworth and S. Peat, *J.*, 1926, 3094.

Reverting now to 2 : 3 : 6-trimethyl glucose (formula V), this sugar passes on methylation to the normal crystalline tetramethyl glucose, which on oxidation yields a liquid tetramethyl gluconolactone differing markedly in properties from the above 2 : 3 : 5 : 6-tetramethyl lactone, and gives rise to a different crystalline phenylhydrazide. This liquid lactone can only be a δ- or 1 : 5-lactone (X), since this is the only alternative available, inasmuch as the remaining positions are occupied by methyl groups. This definitely fixes the constitution of normal crystalline tetramethyl glucose as an amylene oxide (XI).

A second and independent line of argument is based on a comparison of the chemical behaviour of the two series of lactones obtainable from the normal and from the γ-derivatives of glucose, galactose, arabinose, and xylose. The two series of lactones differed essentially both in the rate and in the extent of their hydrolysis in water, as determined by polarimetric data, and, partly, by titration. Those derived from the methylated γ-sugars hydrolysed slowly and very incompletely; those from the normal methylated sugars hydrolysed rapidly and much more completely, and these results are expressed graphically by the authors in a series of curves. Now γ-galactonolactone and γ-arabonolactone give on methylation the same products respectively as those obtained by direct oxidation of tetramethyl "γ"-galactose and trimethyl "γ"-arabinose and therefore the fortuitous use of the term "γ"- in the latter nomenclature happens by coincidence to acquire a structural meaning, and these sugars are 1 : 4- or butylene oxides. On the other hand, the tetramethyl galactonolactone derived from normal tetramethyl galactose has already been shown to be an amylene oxide. Similarly, the normal forms of trimethyl arabinose and trimethyl xylose are known to be amylene oxides and thus give δ- or 1 : 5-lactones, since they pass on oxidation to trimethoxyglutaric acids.

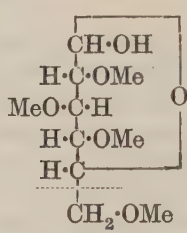
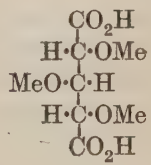
To summarise: Of the four sugars examined, three give methylated "γ"-derivatives which are true butylene oxides. The same three also give methylated normal derivatives which are amylene oxides, leaving only the two methylated glucoses to be allocated. Now the properties of the lactone obtained from crystalline tetramethyl glucose (prepared from α- or β-methylglucoside) are almost indistinguishable from those of the amylene oxide or δ-lactones from methylated normal galactose and arabinose, and thus by analogy the normal crystalline tetramethyl glucose is given the amylene-oxide structure, thus confirming the result already reached from the first line of reasoning.

The difference in the properties of lactones of the two types is again illustrated by the work of P. A. Levene and H. S. Simms,[7]

[7] *J. Biol. Chem.*, 1926, **68**, 737; **A.**, 1025.

who have confirmed the presence of five- and six-membered rings in methylated sugars of different origin.

A third line of argument has also been presented, furnishing a final confirmatory proof. Crystalline tetramethyl glucose (XII) was oxidised [8] with nitric acid and xylotrimethoxyglutaric acid (XIII) was isolated, and consequently by these independent lines of investigation the amylene-oxide structure of α- and β-methylglucosides and crystalline tetramethyl glucose is indicated, and by inference the same structure is applied to free glucose.

(XII.)  (XIII.) 

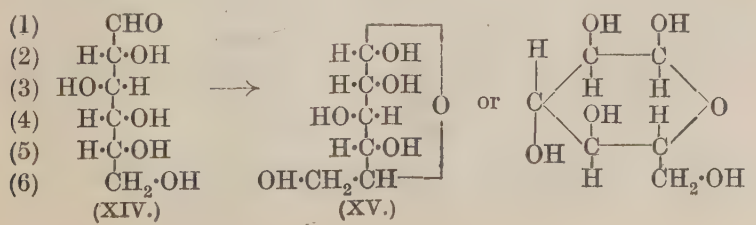
Methylation of rhamnose [9] under a variety of conditions furnishes a normal trimethyl methylrhamnoside of definite structural form. Oxidation of this with nitric acid gives a quantitative yield of *l*-arabotrimethoxyglutaric acid, $CO_2H\cdot[CH\cdot OMe]_3\cdot CO_2H$, and this result can only be interpreted on the basis of the amylene-oxide structure for this methylated sugar. From a comparison of the stereochemical forms of rhamnose, it is suggested,[10] however, that one of these forms is not a normal variety of the sugar and contains a different ring structure, and a similar view is held with regard to one of the stereochemical forms of mannose.

Contrary conclusions as to the structure of methylglucosides are reached, however, by Hudson,[11] who has instituted a comparison of the rotatory relationships of the methylglucosides with those of the methylarabinosides, xylosides, and galactosides. The arguments advanced by this author favour the old formula for the α- and β-methylglucosides. Replying to this criticism, Drew and Haworth [12] question the validity of conclusions based on a comparison of the magnitude of rotatory values displayed by optically active systems so dissimilar as the methylglucosides and arabinosides, since the ring-forming oxygen joins in the first case two asymmetric atoms directly and in the second case only one such atom. Accepting Hudson's lactone rule as true, namely, that the rotation sign tends

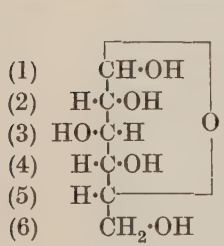
[8] E. L. Hirst, *J.*, 1926, 350; **A.**, 385.
[9] E. L. Hirst and A. K. Macbeth, *ibid.*, p. 22; **A.**, 273.
[10] C. S. Hudson, *J. Amer. Chem. Soc.*, 1926, **48**, 1427; **A.**, 714.
[11] *Ibid.*, p. 1434; **A.**, 714.
[12] *J.*, 1926, 2303; **A.**, 1125.

to be in the positive sense when the lactone ring formation engages a hydroxyl group on the right of Fischer's projection formula, and, conversely, tends to be negative when a hydroxyl group on the left is engaged in ring formation, then it is argued that a parallel significance should be attached to the spatial placing of the ring to the right or the left in the free sugars or their glucosides. This possible extension of Hudson's lactone rule to the sugars proposed by Drew and Haworth can only be tested if the rotatory effect of the reducing group can be eliminated as is the case in the lactones themselves. This can be achieved in those cases where the crystalline α- and β- forms of sugars are already known, since the mean of the specific rotations of these two forms of the same sugar gives the rotatory effect of the remaining carbon atoms. Thus, if the rotation effect of the reducing carbon in the α- and β-modifications be expressed by $+A$ and $-A$ respectively, and all the remaining carbon atoms in the sugar chain be considered as having a rotation $+B$, then the rotation of the α-variety is expressed by $+A+B$, and similarly that of the β-variety by $-A+B$. The sum of these values, halved, gives the rotation effect of B.

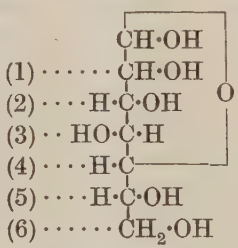
Proceeding in this way it is shown that where the amylene-oxide ring would engage a hydroxyl group on the right of the projection formula the equimolecular mixture of α- and β- forms has a positive rotation, and in the converse case the sign is negative. There appear to be few, if any, exceptions to this rule when authentic data are available, but two cases, mannose and rhamnose, are excluded, since for other reasons the α- and β- forms are considered to be abnormally related. Non-crystalline sugars are clearly excluded from the scope of this survey, as also, but on different grounds, are the simple pentoses, since the amylene-oxide ring in, *e.g.*, xylose and arabinose joins the two terminal carbon atoms, one of which is not asymmetric. Except in the simple pentoses, ring closure is effected by exercising rotational movement round the carbon intermediately situated in the chain, the effect of which is to bring the atoms constituting the ring into one central plane, with its addenda laterally extended. Thus the aldose form of glucose (XIV) changes to the amylene oxide form by the inversion of the groups round C(5), as in (XV).



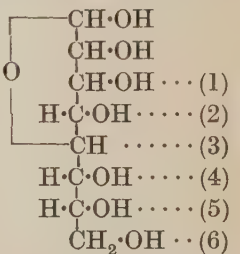
This generalisation is markedly displayed in the case of those monoses prepared by Fischer by ascending the sugar series from the hexoses to the octoses. Thus, whilst the lactone rule holds if the butylene oxide ring is applied to those higher lactones which are intermediate stages in the ascent of the sugars, the adoption of a similar rule breaks down if the derived sugars are regarded as butylene oxides, but holds in all authentic cases if the sugar is considered as amylene-oxidic. For example, the equimolecular mixture of the two glucoheptoses has a positive rotation when the ring engages the hydroxyl group at carbon atom 4 of the glucose chain, but when gluco-octose is reached the rotation is negative, and in this case the hydroxyl group on C(3) is directed to the left.



Glucose.

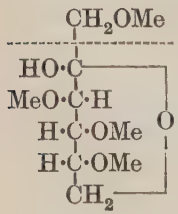


Glucoheptose.

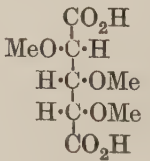


Gluco-octose.

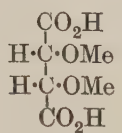
The normal aldoses having been said to conform to the general type of amylene oxides, the characteristic ketose, fructose, is now shown to fall within the same generalisation. The lævorotatory fructose, or lævulose, gives on methylation a crystalline tetramethyl fructose which is similarly lævorotatory. By oxidation with nitric acid, this sugar is degraded to arabotrimethoxyglutaric acid (XVII) and dimethyl *meso*tartaric acid (XVIII), both products being recognised as the crystalline amides.[13] The amylene-oxide formula (XVI) is therefore ascribed to tetramethyl fructose, and presumably also to free fructose. Accompanying these products of oxidation is a crystalline ester to which is given the provisional formula (XIX). It is probable that the degradation product described by previous



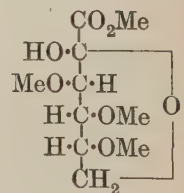
(XVI.)



(XVII.)



(XVIII.)

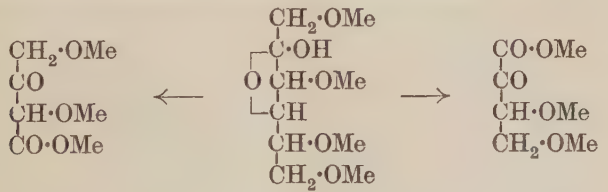


(XIX.)

[13] W. N. Haworth and E. L. Hirst, *J.*, 1926, 1858; **A.**, 1126; C. F. Allpress, *ibid.*, p. 1720; **A.**, 942.

authors as the diethyl ester of dimethoxyhydroxyglutaric acid is the monoethyl ester corresponding to (XIX), and accordingly this earlier claim [14] to have established the butylene-oxide structure of normal fructose is disputed.

If this dethronement of the older fructose formula from its position in the ketose series be accepted, the implications are as important as those resulting from the revision of the older glucose formula in the series of the aldoses. In the same paper describing the experimental proof of the new structural formula of fructose, Haworth and Hirst have also revised the constitution previously assigned to tetramethyl γ-fructose, the dextrorotatory sugar isolated from methylated sucrose, raffinose, and inulin. These authors propose the butylene-oxide formula for derivatives of γ-fructose on the analogy of the structure already assigned by one of them to the γ-aldoses. Against this view, G. McOwan [15] has revived the propylene-oxide formula for tetramethyl γ-fructose, and has adduced evidence, largely critical of earlier work, in support of his proposal. It is suggested that the primary product isolated by oxidation of tetramethyl γ-fructose with nitric acid is not a trimethoxyvalerolactone, but a keto-ester (A) or (B), whence it is argued that the original sugar is a propylene oxide as represented by (C). The keto-ester (A) or (B) is not definitely characterised, and it would seem that the isolation of a product (A) would equally well satisfy the requirements of a butylene-oxide structure.



(A) (C) (B)

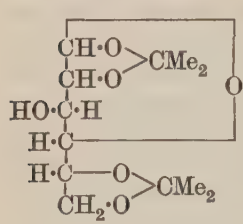
Whilst the arguments already outlined may be said to have established the amylene-oxide structure of the representative reference compounds, α- and β-methylglucosides, crystalline tetramethyl glucose, etc., it is urged by several authors [16] that the unsubstituted glucose has not necessarily the same oxide ring. Doubt is thus cast on the inter-relationship of α- and β-glucoses with α- and β-methylglucosides, which was considered to have been firmly established by E. F. Armstrong. The reason advanced for this uncertainty is the existence of glucose diacetone, which has been shown to have the

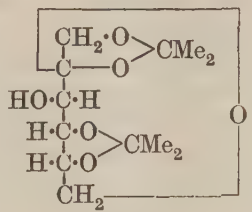
[14] J. C. Irvine and J. Patterson, *J.*, 1922, **121**, 2696.

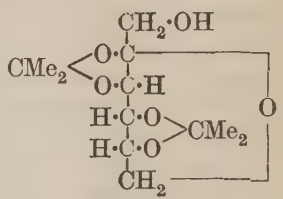
[15] *J.*, 1926, 1742; **A.**, 941.

[16] K. Freudenberg and K. Smeykal, *Ber.*, 1926, **59**, 100; **A.**, 274; P. A. Levene and H. S. Simms, *J. Biol. Chem.*, 1926, **68**, 737; **A.**, 1025.

butylene-oxide structure (D),[17] since it gives, after methylation and elimination of the acetone residues, 3-methyl glucose. The latter sugar yields the same osazone as the monomethyl fructose derived from α-fructose diacetone, which has therefore the constitution (E).

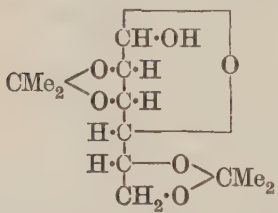

(D)

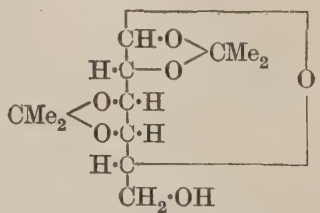

(E)


(F)

The isomeric β-fructose diacetone is assigned the constitution (F), which differs structurally [18] from that of the α-isomeride, and not merely stereochemically.

Now, as glucose passes so readily into the compound (D) by simple condensation with acetone, the inference is drawn that the butylene-oxide ring in the diacetone derivative may have been pre-formed in the original glucose, which in such case would retain its old position as a butylene-oxide sugar despite the amylene-oxide structures of α- and β-methylglucoside and crystalline tetramethyl glucose. This hypothesis receives some support [19] from the analogy of the diacetone derivative of mannose, to which is allocated also a butylene-oxide structure (G).


(G)


(H)

On the other hand, to galactose diacetone the constitution (H) is definitely assigned.[20]

From a consideration solely of the oxide-ring structures of the diacetones it is suggested that, whilst fructose and galactose possess amylene-oxide rings, mannose and glucose, on the other hand,

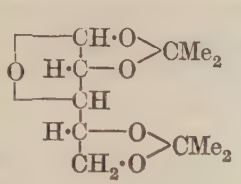
[17] J. C. Irvine and J. Patterson, *J.*, 1922, **121**, 2146.

[18] H. Ohle, I. Koller, and G. Berend, *Ber.*, 1925, **58**, 2577; **A.**, 1926, 150.

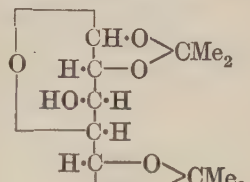
[19] H. Ohle and G. Berend, *ibid.*, p. 2590; **A.**, 1926, 150; K. Freudenberg and A. Wolf, *ibid.*, 1926, **59**, 836; **A.**, 601; J. C. Irvine and A. F. Skinner, *J.*, 1926, 1089; **A.**, 714.

[20] K. Freudenberg and K. Smeykal, *Ber.*, 1926, **59**, 100; **A.**, 274.

contain the butylene-oxide rings. This argument is only valid if it be assumed that the ring systems of the parent sugars remain unimpaired by the entry of acetone groups in the adjoining hydroxyl positions. There is, however, much reason to doubt the accuracy of this assumption.[21] It appears to be the accepted rule that acetone, like boric acid, condenses with *cis*-hydroxyl groups in adjoining carbon atoms in cyclic systems,[22] and unless this principle is abrogated, the structure of xylose diacetone should be (J), which is seen to present yet another type of sugar ring—a



(J)



(K)

propylene oxide—which would be the first authentic case of the existence of a sugar derivative in a third structural form, since two varieties, the normal and the γ-form of xylose, are also known. If this should prove to be the case, or alternatively, if the second form of a galactose diacetone (K) should be isolated differing from (H) in having a butylene-oxide ring, then the truth with regard to the formation of acetone derivatives of sugars will be that acetone condenses with appropriately situated hydroxyl groups in any sugar regardless of any pre-formed sugar ring. The ring system in the parent sugar will then have been shown to adjust itself to that position left open after the entry of acetone residues by a process of preferential selection. A reason would thus be provided for the existence of acetone-sugars containing rings of a variety of types, formed quite irrespectively of the original ring system in the parent free sugar. The shift in the position of attachment of the oxide ring in glucose during its condensation with acetone would, indeed, correspond with that which is known to occur, for example, when amylene-oxidic galactose condenses at room temperature with methyl alcohol to give a butylene-oxidic γ-methyl galactoside.

Monosaccharides.

From the point of view of the possible synthesis of α-glucosides, the preparation[23] of β-chloro-3 : 4 : 6-triacetyl-2-trichloroacetyl-

[21] H. Ohle and K. Spencker, *Ber.*, 1926, **59**, 1836; **A.**, 1126.

[22] J. Böeseken and Mlle. A. Julius, *Rec. trav. chim.*, 1926, **45**, 489; **A.**, 818. Compare also earlier work.

[23] P. Brigl and H. Keppler, *Ber.*, 1926, **59**, 1588; **A.**, 941.

glucose is of importance, since this readily gives rise to α-methyl-glucoside on boiling with methyl alcohol in presence of silver carbonate. The better-known halogen derivative, α-bromotetra-acetylglucose (tetra-acetyl-glucosidyl bromide), yields only β-glucosides under similar conditions. In this connexion, the isolation of β-chlorotetra-acetylglucose [24] as a pure crystalline compound is of significance, but the preparation of this reagent requires the application of most stringent conditions. The preparation of a stable form of glucose [25] is reported which is said to contain a different ring structure from either the normal or the usual γ-type. Derivatives of this variety have been isolated as a penta-acetate and a trimethyl sugar which are said to possess considerable stability of grouping and to contain a hexylene-oxide ring.

A new aminohexose,[26] containing the amino-group in position 3 and therefore differing structurally from glucosamine, has been prepared from glucose diacetone, whilst 3-chloro-glucose [27] also has been obtained from the same source by the agency of phosphorus pentachloride and sodium carbonate, a method which pays tribute to the remarkable stability of the combined acetone residues in glucose diacetone. A study of the conditions [28] of entry of substituted groups into glucose monoacetone is also contributed, showing that position 6 is first attacked by reagents, and if this is already substituted, then position 5 is preferred, since the oxide ring in this acetone compound engages the positions 1 : 4.

In continuation of previous work on the preparation of sugar carbonates, a series of five derivatives of arabinose and xylose containing carbomethoxy- and carbethoxy-groups is reported.[29]

Improved experimental conditions for the preparation of the simple oxidation products of sugars are described.[30] These include *l*-arabonic, *l*-mannonic, and *l*-gluconic acids and the related lactones. The extension of this work to the " uronic " acids will be welcomed in view of the study of the structure of the pectins. The supposed semicarbazones of galacturonolactone and mannuronolactone are now shown to be semicarbazides of the unoxidised acids. A synthesis of sarcosine glucoside is described,[31] and the action of carbamide

[24] H. H. Schlubach, *ibid.*, p. 840; **A.**, 600.
[25] H. Pringsheim and S. Kolodny, *ibid.*, p. 1135; **A.**, 822.
[26] K. Freudenberg, O. Burkhart, and E. Braun, *ibid.*, p. 714; **A.**, 601.
[27] J. B. Allison and R. M. Hixon, *J. Amer. Chem. Soc.*, 1926, **48**, 406; **A.**, 386.
[28] H. Ohle and E. Dickhäuser, *Ber.*, 1925, **58**, 2593; **A.**, 1926, 151.
[29] W. N. Haworth and W. Maw, *J.*, 1926, 1751; **A.**, 940.
[30] H. Kiliani, *Ber.*, 1925, **58**, 2344; 1926, **59**, 1469; **A.**, 1926, 51, 940.
[31] K. Maurer, *ibid.*, 1926, **59**, 827; **A.**, 602.

on glucose, fructose, and mannose has been carefully studied, leading to an improved method of preparing glucoseureide.[32] Modified conditions for the preparation of hexoseanilides are also reported.[33]

A series of interesting sugar nitrates [34] which are crystalline has been prepared from glucosan, comprising 2 : 3 : 4-trimethyl glucose 1 : 6-dinitrate, which can be converted into the corresponding 2 : 3 : 4-trimethyl methylglucoside 6-mononitrate; also the corresponding triacetyl glucose dinitrate and tetra-acetyl glucose mononitrate, the latter giving a tetra-acetyl glucose on hydrolysis. Other crystalline compounds of great interest are triacetyl methylglucoside 6-mononitrate, which hydrolyses to the triacetyl methylglucoside, and triacetyl methylglucoside-6-isohydrin.

The occurrence of a thio-sugar in the adenine nucleoside from yeast is reported. This sugar also contains a methyl group and appears to be a derivative of a ketose.[35]

Methylation of diethylmercaptoglucose, first by methyl sulphate and then by Freudenberg's method, yields the completely methylated derivative, and treatment of this with mercuric chloride leads to the isolation of pentamethyl glucose.[36] This is noteworthy as the first example of the preparation of a true sugar-aldehyde. The behaviour of the latter with methyl alcohol is of marked interest in that it passes to the dimethylacetal with excessive ease. These properties illustrate the difference between a heterocyclic-ring type of sugar of the usual kind and the simplest open-chain type, and it is to be hoped that the study of this unique sugar compound will be pursued.

Mutarotation and Classification.

Lowry has continued his classical studies in dynamic isomerism and has measured the velocity of mutarotation of tetramethyl glucose and of tetra-acetyl glucose in aqueous acetone. The significant result emerges that acetone diminishes the catalytic activity of water.[37] Thus in a 50% mixture of water and acetone the velocity of mutarotation of tetramethyl glucose is about 20% of that in pure water. The catalytic activity of the water is not in proportion to its total concentration and is not a simple linear

[32] A. Hynd, *Biochem. J.*, 1926, **20**, 195; **A.**, 501; B. Helferich and W. Kosche, *Ber.*, 1926, **59**, 69; **A.**, 273.

[33] C. N. Cameron, *J. Amer. Chem. Soc.*, 1926, **48**, 2233, 2737; **A.**, 1026, 1228.

[34] J. W. H. Oldham, *J.*, 1925, **127**, 2840; **A.**, 1926, 151.

[35] P. A. Levene and H. Sobotka, *J. Biol. Chem.*, 1925, **65**, 551; **A.**, 1926, 52.

[36] P. A. Levene and G. M. Meyer, *ibid.*, 1926, **69**, 175; **A.**, 1026.

[37] G. G. Jones and T. M. Lowry, *J.*, 1926, 720; **A.**, 481.

function of its activity as measured by its partial vapour pressure above the solution.

A maximum velocity of mutarotation for glucose, twenty times that shown in pure water, is attained by using a mixture of pyridine with twice its weight of water as solvent.[38] In the absence of water, pyridine and also cresol have by themselves no appreciable catalytic properties, but a dry mixture of two parts of cresol and one part of pyridine is twenty times more active than is water in promoting the mutarotation of tetramethyl glucose. This increased activity is attributed to the amphoteric character of the mixed solvent, and the conclusion is reached that to promote a change in position of an atom within the sugar molecule it is necessary to supply a medium into which a proton can escape and from which a proton can be provided. This hypothesis is supported by the observation that the only substances known to act as catalysts for the mutarotation of sugars possess either acidic or basic properties, or both. Ethyl acetate or acetone fails to accelerate this change even in presence of water, and in the dry condition these solvents and also pyridine are quite inert.

Alcohols can be regarded as amphoteric in the sense that they can liberate either hydrogen or hydroxyl to suitable chemical reagents, although they do not necessarily possess sufficiently strong acidic and basic properties to react as complete catalysts for the mutarotation of sugars. On this assumption a series of experiments has been conducted with the use of the purest methyl alcohol. It was recorded [39] that methyl alcohol, mixed with three times its weight of cresol, gave a maximum coefficient which was ten times that of methyl alcohol alone, and further, that methyl alcohol mixed with two-thirds its weight of pyridine gave a value twenty times as great as the former mixture. It is concluded that since methyl alcohol is sufficiently acidic to form a complete catalyst with pyridine, and sufficiently basic to form a complete catalyst with cresol, it must also be able to function alone as an amphoteric solvent to promote mutarotation of sugars. The velocity in ethyl alcohol is eighty times less than the velocity in water. Other experiments show that neutral salts largely affect the speed of mutarotation of α- and β-glucose, which display their minimum stability at about the same p_H value. It does not follow, however, that the dissociation constants of the sugars correspond. Apparently there is no evidence for the existence of a third undissociated intermediate form, a conclusion which is of value in considering the

[38] T. M. Lowry and I. J. Faulkner, *J.*, 1925, **127**, 2883; **A.**, 1926, 148.

[39] I. J. Faulkner and T. M. Lowry, *J.*, 1926, 1938; **A.**, 1026; H. von Euler and I. Hedström, *Arkiv Kemi, Min., Geol.*, 1926, **9**, No. 17, 1; **A.**, 714.

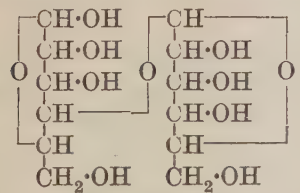
oxide-ring structure of free glucose. The region of maximum stability of glucose at 20° is p_H 4·83 and the value of the specific reactivity of the dextrose anion is 66. The curves showing mutarotation plotted against p_H indicate that glucose functions as a very weak acid and also as a very weak base.[40]

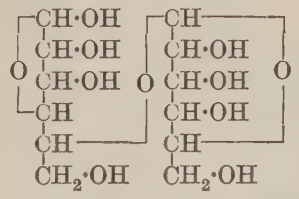
It is suggested that Fischer's classification of the *d*- and *l*-series of the sugars breaks down in the case of arabinose, and that for the normal forms of the aldoses the configuration of the middle group of the oxide ring (carbon atom 3) is the deciding factor in this classification. According to this view,[41] the natural arabinose belongs to the *d*-series instead of to the *l*-series.

Disaccharides.

The constitution of maltose has been reviewed during the year and three papers have been published dealing with the nature of the oxide ring and with the position taken up by the biose linking. The diagnosis of the trimethyl glucose separated from the cleavage products of heptamethyl methylmaltoside now establishes the positions of the methyl groups, this fragment being recognised as 2 : 3 : 6-trimethyl glucose.[42] The effect of the two papers communicating this result is to overturn Fischer's structural formula for maltose, which had been supported by the previous diagnosis of the above fragment as 2 : 3 : 4-trimethyl glucose. Since this new experimental work does not, however, differentiate between the alternative formulæ (I) and (II) for maltose, the determination of the structure of this disaccharide remained inconclusive.

(I.)





(II.)

The problem was finally solved [43] by application of experimental methods which were independent of the solution based on the diagnosis of the above trimethyl glucose. Maltose was oxidised to maltobionic acid, which gave on methylation methyl octamethylmaltobionate (III). By the hydrolysis of this product, crystalline 2 : 3 : 5 : 6-tetramethyl γ-gluconolactone (IV) was isolated along with

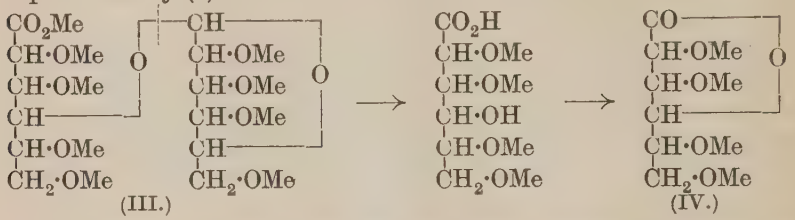
[40] H. von Euler and A. Ölander, *Z. anorg. Chem.*, 1926, **152**, 113; **A.**, 580.

[41] J. G. Maltby, *J.*, 1926, 1629; **A.**, 822; C. J. de Wolff, *Chem. Weekblad*, 1926, **23**, 353; **A.**, 940.

[42] J. C. Irvine and I. M. A. Black, *J.*, 1926, 862; **A.**, 602; C. J. A. Cooper, W. N. Haworth, and S. Peat, *ibid.*, p. 876; **A.**, 602.

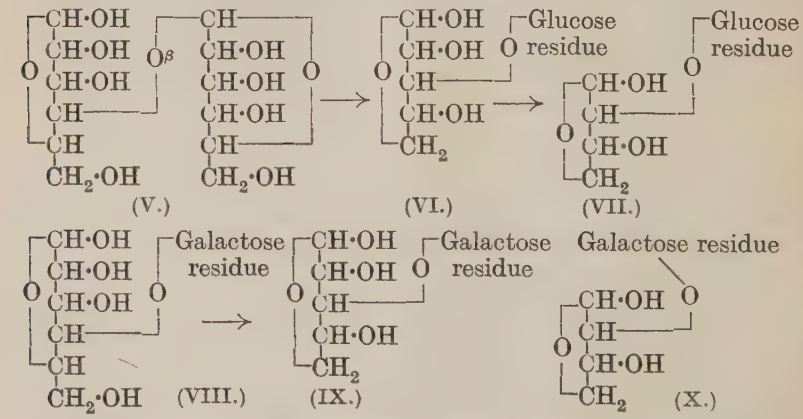
[43] W. N. Haworth and S. Peat, *ibid.*, p. 3094.

the expected 2 : 3 : 4 : 6-tetramethyl glucose. The recognition of the structure of this lactone left no doubt as to the position occupied by the biose linking in maltose, the constitution of which is now represented by (I).



(III.) (IV.)

This result ascribes to maltose the same structural formula as is given to cellobiose,[44] the difference being that whereas the former is a glucose-α-glucoside the latter is a glucose-β-glucoside. Furthermore, a direct determination of constitution which excludes the use of methylated products confirms this cellobiose structure. Cellobiose was degraded [45] through the octa-acetate of cellobiononitrile to the gluco-arabinose (VI), which yielded three isomeric crystalline hepta-acetyl derivatives and also a crystalline sugar. Finally, the degradation to a glucotetrose (VII) was reached, and this product was found to be incapable of forming an osazone. This circumstance is ascribed to the location of the biose linking at the second carbon atom of the tetrose unit, and since this linking is presumably unimpaired by the successive stages in the degradation, the biose linking in cellobiose is attached to the fourth carbon atom in the reducing hexose residue. It follows, therefore, that cellobiose has the constitution (V).



(V.) (VI.) (VII.) (VIII.) (IX.) (X.)

[44] W. N. Haworth and E. L. Hirst, *J.*, 1826, p. 1858; **A.**, 1126; W. Charlton, W. N. Haworth, and S. Peat, *ibid.*, p. 89; **A.**, 273.

[45] G. Zemplén, *Ber.*, 1926, **59**, 1254; **A.**, 822.

The application by this author of a similar method to the case of lactose led to the isolation of a galacto-arabinose (IX) which yielded a phenylosazone, and also of a galacto-erythrose (X) which was incapable of yielding an osazone. From these experiments, it follows that lactose has the constitution (VIII). These results confirm the constitutional formulæ already ascribed to cellobiose and lactose by earlier workers.[46]

Closely associated with the question of the relationship of cellobiose to the structure of cellulose is the isolation of cello*iso*biose and cellotriose from the polysaccharide. Revised details for the isolation of these cleavage fragments are given,[47] the properties having previously been ill-defined. The disaccharide which has been designated cello*iso*biose is considered to represent a constituent part of the cellulose molecule, but its complete characterisation and its structure remain as a problem for the future. The hypothesis [48] that cellobiose and cello*iso*biose should be considered as one structurally identical pair and maltose and *iso*maltose as a second such pair does not seem to be warranted by the facts already observed.[49]

Fischer's *iso*maltose, prepared by the action of acid on glucose, is shown to be a mixture containing also gentiobiose. The purified *iso*maltose has been characterised and its synthesis achieved from di-lævoglucosan.[50] Gentiobiose has already been synthesised by enzyme action on glucose, but a new synthesis [51] is now reported by the use of methods which leave the constitution open to no doubt.

Condensation of 2 : 3 : 4-tribenzoylglucosyl fluoride (XI) is effected with acetobromoglucose (XII) in presence of silver oxide. From the crystalline product the acyl groups are removed by methyl-alcoholic ammonia, yielding gentiobiosyl fluoride, and this gives gentiobiose on boiling in aqueous solution with calcium carbonate. The disaccharide was identified by its octa-acetate and its osazone, and its synthesis by these methods confirms the

[46] G. Zemplén, *Ber.*, 1926, **59**, 2402; **A.**, 1229; W. N. Haworth and Miss G. C. Leitch, *J.*, 1918, **113**, 189; W. Charlton, W. N. Haworth, and S. Peat, *loc. cit.*

[47] H. Ost, *Z. angew. Chem.*, 1926, **39**, 1117; **A.**, 1127.

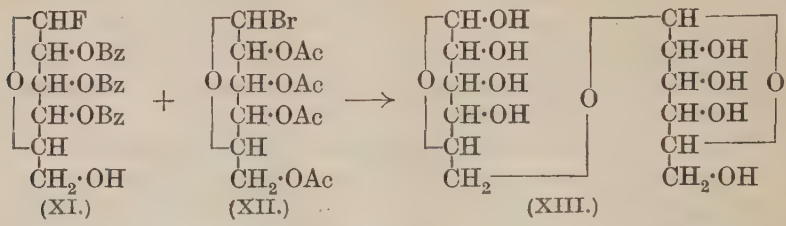
[48] J. C. Irvine and Black, *loc. cit.*

[49] W. N. Haworth and S. Peat, *loc. cit.*

[50] A. Georg and A. Pictet, *Helv. Chim. Acta*, 1926, **9**, 612; **A.**, 823; A. Pictet and A. Georg, *Compt. rend.*, 1925, **181**, 1035; **A.**, 1926, 152; A. Georg and A. Pictet, *Helv. Chim. Acta*, 1926, **9**, 444; **A.**, 602; H. Pringsheim, J. Bonde, and J. Leibowitz, *Ber.*, 1926, **59**, 1983; **A.**, 1127; J. V. Isajev, *Chem. Listy*, 1926, **20**, 251; **A.**, 714; H. Berlin, *J. Amer. Chem. Soc.*, 1926, **48**, 1107; **A.**, 602.

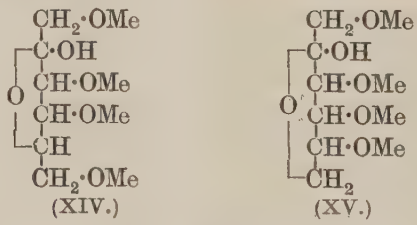
[51] B. Helferich, K. Bäuerlein, and F. Weigand, *Annalen*, 1926, **447**, 27; **A.**, 386; B. Helferich, W. Klein, and W. Schäfer, *ibid.*, p. 19.

constitution (XIII) already assigned to gentiobiose by earlier workers.[52]



A striking example of a Walden inversion which emphasises the need for caution in selecting methods of investigation of the sugars is encountered in the interaction of aluminium chloride and lactose octa-acetate.[53] Under specified conditions, a 20% yield of the chlorohepta-acetate of a new disaccharide, neolactose, is obtained, which is recognised as *d*-galactosido-*d*-altrose. The reaction involves the inversion of the groups 2 and 3 in the reducing glucose residue in lactose. This is not a solitary instance, since a similar inversion [54] has been effected also with cellobiose.

The constitution assigned to sucrose in earlier investigations is adversely affected by the new experiments already commented on in this Report (p. 80), which invalidate the oxide-ring structure applied to normal fructose. The methylated representative of the latter sugar is crystalline tetramethyl fructose, and the constitution formerly assigned to it by Irvine and Patterson [55] on the basis of its oxidation was (XIV).



This is considered to be erroneous and the new constitution (XV) is now allocated by Haworth and Hirst [56] to this important reference compound. In the latter paper, it is indicated that the

[52] W. N. Haworth and B. Wylam, *J.*, 1923, **123**, 3120.

[53] A. Kunz and C. S. Hudson, *J. Amer. Chem. Soc.*, 1926, **48**, 1978, 2435; **A.**, 941, 1127.

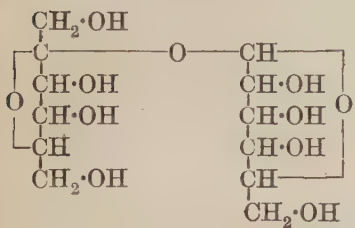
[54] C. S. Hudson, *ibid.*, p. 2002; **A.**, 941.

[55] *J.*, 1922, **121**, 2696; W. N. Haworth and E. L. Hirst, *J.*, 1926, 1858; **A.**, 1126.

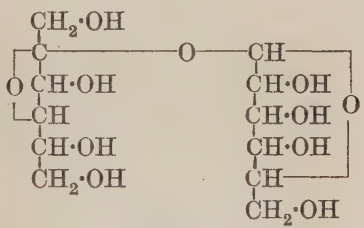
[56] *Loc. cit.*

interpretation of earlier results on the oxidation of the isomeric fructose derivative, the liquid tetramethyl γ-fructose, must also be erroneous, since the formula (XV) now definitely reserved for the normal fructose derivative had previously been applied to this sugar by Haworth and W. H. Linnell.[57]

The readjustment of the oxide-ring formula of tetramethyl γ-fructose, a product derived from methylated sucrose, remains to be effected. The constitution (XVI) is tentatively ascribed to sucrose by Haworth and Hirst, indicating the fructose residue as a butylene oxide. A criticism of the earlier sucrose formula is presented also by McOwan.[58] This author suggests that the liquid degradation product obtained from tetramethyl γ-fructose is a ketodimethoxypropanecarboxylic ester, and on the basis of this interpretation the formula (XVII) is suggested for sucrose, which represents the fructose residue as a propylene oxide. This conclusion appears to be based, however, on the older formula for normal tetramethyl fructose.



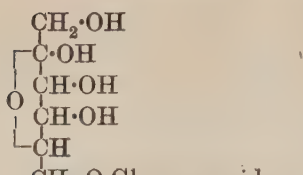
(XVI.)



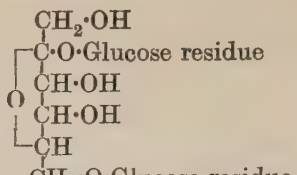
(XVII.)

Turanose and melezitose have been the subjects of a constitutional study by two authors and it appears to be established that the latter trisaccharide has its three hexose units arranged in the sequence glucose—fructose—glucose.[59] Completely methylated melezitose undergoes hydrolysis with acetic acid to give normal tetramethyl glucose and a product which on methylation gives octamethyl turanose. Hydrolysis of the latter with mineral acid leads to normal tetramethyl glucose and a trimethyl γ-fructose, which is considered to be the 1 : 3 : 4-isomeride. The author [60] interprets these results on the basis of the new butylene-oxide structure for the γ-fructose unit, turanose being indicated by the symbol (XVIII) and melezitose by (XIX).

[57] *J.*, 1923, **123**, 294.
[58] G. McOwan, *J.*, 1926, 1737; **A.**, 941.
[59] R. Kuhn and G. E. von Grundherr, *Ber.*, 1926, **59**, 1655; **A.**, 1127.
[60] G. Zemplén, *ibid.*, p. 2230, 2539.



(XVIII.)



(XIX.)

Starch.

Although maltose is the characteristic product of the enzyme cleavage of starch, this disaccharide does not appear to be formed by either the acid hydrolysis or the acetolysis of the polysaccharide. On the contrary, two quite different acetates are produced according as the inner or the outer substance of the starch granule is subjected to acetolysis. The first of these, amylose, yields the acetate of dihexosan, an anhydro-disaccharide which can be hydrolysed to give the disaccharide amylobiose,[1] whilst amylopectin, the second starch substance, yields initially the acetate of trihexosan. Both dihexosan and trihexosan are also obtained by heating amylose and amylopectin, respectively, with glycerol.[2] Furthermore, hydrolysis of the starches with cold concentrated hydrochloric acid leads to the isolation of the reducing sugars amylobiose and amylotriose,[3] which are characterised through their osazones as a disaccharide and a trisaccharide, and amylobiose appears to be quite differently constituted from maltose.

Again, whilst under special conditions starch can be completely degraded by ferments to maltose, the more usual procedure yields 75% of the latter biose along with a limiting product, a dextrin, which is now identified with trihexosan,[4] and by the use of a malt-amylose of a special character, the inner starch material, amylose, gives rise to dihexosan as the limiting product.[5] The relationship of trihexosan to dihexosan is apparent in that from the former, by the action of emulsin,[6] dihexosan can be isolated along with the polymeride tetrahexosan. Then, by the agency of either mineral acid or barley diastase, dihexosan is converted into maltose. If dihexosan were to be identified with anhydromaltose as is suggested, then the internal structure of these products could be easily eluci-

[1] H. Pringsheim, *Ber.*, 1926, **59**, 3010.

[2] A. Pictet and R. Jahn, *Helv. Chim. Acta*, 1922, **5**, 640; *A.*, 1922, i, 987; H. Pringsheim and K. Wolfsohn, *Ber.*, 1924, **57**, 887; *A.*, 1924, i, 714.

[3] H. Pringsheim, *Ber.*, 1924, **57**, 1581.

[4] H. Pringsheim and A. Beiser, *Biochem. Z.*, 1924, **148**, 336.

[5] K. Sjöberg, *Ber.*, 1924, **57**, 1251; **A.**, 1924, i, 1169.

[6] A. Pictet and R. Salzmann, *Helv. Chim. Acta*, 1925, **8**, 948; **A.**, 1926 52; compare *A.*, 1924, i, 1288.

dated, since the constitution of maltose is now finally decided. That there must be some close connexion between these products and maltose is confirmed, inasmuch as hexahexosan is converted by the agency of acetyl bromide into hepta-acetyl maltose,[7] and is also transformed directly into maltose by amylase or emulsin. Some progress has been made in the study of these breakdown products. For example, trihexosan undergoes partial methylation,[8] giving a monomethyl derivative which is considered to be homogeneous. Since this yields on hydrolysis 6-monomethyl glucose, proving that the terminal primary alcohol residue in the associated glucoses is not concerned in the internal linkings, the isolation of this product renders doubtful the formula, first proposed by Pringsheim and Leibowitz,[9] containing internal 1 : 6-oxide rings.

A quantitative conversion of starch, amylose or amylopectin, into glucose occurs by the use of a combination of pancreatic and malt amylases;[10] whilst a technical ferment, "biolase," transforms starch, but not amylobiose, into glucose, accompanied by a small amount of a reducing trisaccharide[11] which may be identical with the β-glucosidomaltose obtained by Ling and Nanji, although the behaviour of the latter towards enzymes is not in agreement with previous results. The view that starch, when purified, can be hydrolysed by salts, amino-acids, and peptones is now said to be erroneous.[12]

Amylobiose is intimately related to dihexosan, and is now obtainable also through α-tetra-amylose. The methylation[13] of amylobiose seems to be arrested when only six methyl groups have been introduced, and that this is an example of steric hindrance only is suggested in that one further hydroxyl residue can be protected by introducing an acetyl group. Hydrolysis of hexamethyl amylobiose succeeds only in establishing the structure of one half of the molecule, since crystalline 2 : 3 : 4 : 6-tetramethyl glucose was isolated; the remaining residue resembles a 3-monomethyl methylglucoside which behaves rather like a γ-sugar derivative. The constitution of this interesting biose is thus nearing solution.

The relationships of dihexosan and amylobiose to the new

[7] P. Castan and A. Pictet, *ibid.*, p. 946; **A.**, 52.

[8] R. Kuhn and W. Ziese, *Ber.*, 1926, **59**, 2314; **A.**, 1230.

[9] *Ber.*, 1924, **57**, 884; *A.*, 1924, i, 714.

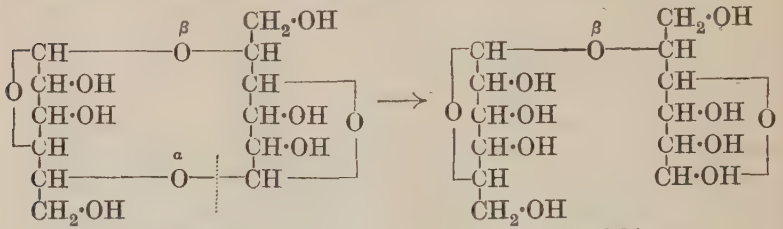
[10] H. Pringsheim and J. Leibowitz, *Ber.*, 1926, **59**, 991; **A.**, 715; R. Kuhn, *Ber.*, 1924, **57**, 1965; *A.*, 1925, i, 11; *Annalen*, 1925, **443**, 1; *A.*, 1925, i, 636.

[11] H. Pringsheim and E. Schapiro, *Ber.*, 1926, **59**, 996; **A.**, 715.

[12] K. Takane, *Biochem. Z.*, 1926, **175**, 241; **A.**, 1059.

[13] H. Pringsheim and A. Steingroever, *Ber.*, 1926, **59**, 1001; **A.**, 715.

structural formula for maltose have been considered, and adopting the revised formulæ for glucose and γ-glucose, Pringsheim [14] advances the tentative suggestions :



Dihexosan. Amylobiose.

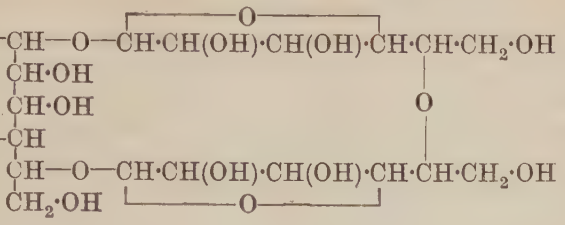
Maltose is regarded as a transformation product of dihexosan or trihexosan involving hydrolysis and rearrangement of the oxide rings, and thus the occurrence of maltose as an essential residue in the starch molecule is considered improbable. In view of the fundamental discoveries recorded in the ensuing section dealing with the elementary unit of cellulose, Pringsheim hesitates to apply the above results in the sense of attributing to either dihexosan or trihexosan the character of the ultimate unit of starch. The latter hypothesis is doubtful for other reasons also,[15] depending on the application of Hudson's views to the stereochemical relationships of these products. The synthesis of starch in nature is attributed to the formation of a labile glucose having the property of directly assimilating carbon dioxide.

Earlier experiments on the investigation of methylated starch [16] are supplemented by the preparation of a completely methylated trimethyl starch [17] which is found to undergo conversion into 2 : 3 : 6-trimethyl methylglucoside. Alternative possibilities for the molecular unit of starch are discussed and in the view of the authors this unit must contain nine or a multiple of nine hydroxyl groups. The simplest unit is thus considered to be a trihexosan or a hexahexosan, and suggested formulæ, *e.g.* (XX), are communicated. The same authors consider that maltose residues occur in the starch complex, and a formula for maltose differing structurally from cellobiose is adopted (compare p. 88). Thus if cellobiose is given an amylene-oxide structure, maltose is said to be constituted on the basis of the presence of a butylene-oxide group in the reducing hexose residue. These views differ essentially from those of Pringsheim, who regards trihexosan and dihexosan as containing

[14] *Ber.*, 1926, **59**, 3012.
[15] H. Pringsheim and J. Leibowitz, *Ber.*, 1925, **58**, 2808; **A.**, 1926, 275.
[16] *Ann. Report*, 1922, **19**, 81.
[17] J. C. Irvine and J. Macdonald, *J.*, 1926, 1502; **A.**, 823.

no pre-formed maltose groupings, and deprecates the identification of the hexosans with the fundamental unit of starch.

(XX.)



Cellulose.

Experiments of the greatest significance in relation to the constitution of cellulose are reported by Hess and Pringsheim and their co-workers. A redetermination of the molecular weight of cellulose diacetate in an acetic acid solution, from which dissolved oxygen is eliminated by a vacuum, gives a mean value corresponding closely with that required for a glucose-anhydride diacetate.[18] This value remains constant for some days and then gradually increases to infinity. There appears to be no evidence of the intermediate formation of the dimeride, $(C_6H_{10}O_5)_2$, and the material isolated from the solutions is identical with the initial crystalline substance, undergoing the same sequence of changes when redissolved. This behaviour is not restricted to the cellulose diacetate, but extends also to crystalline cellulose triacetate and lichenin triacetate. Inasmuch as these cellulose acetates are convertible into pure cellulose, and this again into acetates without apparent change in structure, these results furnish strong evidence in support of the view of Hess that the structure of cellulose may be represented by a glucose anhydride which, differing from other glucosans, is capable of swelling and is sparingly soluble in water.

When cellulose triacetate is heated in presence of naphthalene at 235°, the molecular weight is diminished to the value of 288, corresponding with the triacetate of anhydroglucose.[19] This diminution in complexity is accompanied by increased solubility in acetone and by a fall in viscosity, although there is no change in rotation. Removal of the acetyl groups discloses an anhydroglucose which is termed cellosan and is soluble in water. At 73—80°, the molecular weight is in agreement with the simple formula $C_6H_{10}O_5$.

Similarly, lichenin acetate is transformed by an analogous

[18] K. Hess and G. Schultze, *Annalen*, 1926, **448**, 99; **A.**, 715; K. Hess, *Koll.-Chem. Beih.*, 1926, **23**, 93; **A.**, 1127.

[19] H. Pringsheim, J. Leibowitz, A. Schreiber, and E. Kasten, *Annalen*, 1926, **449**, 163; **A.**, 942.

procedure into lichosan,[20] which also is a glucose anhydride. The close relationship of lichenin to cellulose is apparent from the conversion of the former into cellobiose by ferments. Moreover, cellulose hydrate, oxycellulose, generated from viscose by permanganate, and hydrocellulose, obtained by reduction of viscose, all give Röntgen diagrams identical with that of lichenin, thus proving that these products have the same crystalline constituents.[21] The conversion of cellulose into lichenin (viscose cellulose) is regarded as a change of modification only. Cellosan and lichosan are considered to be the elementary units of cellulose and lichenin, and thus these polysaccharides are regarded as the products of associated glucose anhydrides, a hypothesis which was previously advanced on the basis of the experimental work of Hess [22] on the nature of the copper-ammine solutions of cellulose. Cellosan appears to undergo reassociation in solution, and it is significant that the specific rotations of cellulose and cellosan are identical in similar solvents, as are also the rotations of lichenin and lichosan. The reassociation of the elementary units thus seems to call into play no readjustment of grouping or of intra-molecular valency,[23] and this feature provides abundant ground for speculation as to the nature of the forces promoting molecular aggregation.

Considerable light is thrown on this problem by the study of the polymerisation of formaldehyde. Staudinger has isolated a long series of oxymethylene diacetates [24] by the action of acetic anhydride on polymerised formaldehyde. Nineteen apparently individual products were recognised of the general type $CH_3 \cdot CO \cdot [O \cdot CH_2]_x \cdot O \cdot CO \cdot CH_3$, in which the value of x varies from 1 to 22, most of these being low-melting solids. A corresponding series of oxymethylene-dimethyl ethers has also been isolated in which the magnitude of x ranges from 6 to 75. This study is supplemented by the consideration of the general problem of polymerisation as applied to vinyl derivatives, styrene, and caoutchouc.

The acetolysis of cotton cellulose, if allowed to proceed to a stage immediately preliminary to the formation of cellobiose octa-acetate, gives an amorphous powder which is soluble in organic media and dextrorotatory. This was subjected to deacetylation and methylation, and the main product consisted of a colourless glass which was recognised as essentially a tri(trimethyl 1 : 4-anhydro-glucose)

[20] H. Pringsheim, *Ber.*, 1926, **59**, 3008.
[21] E. Ott, *Helv. Chim. Acta*, 1926, **9**, 31; **A.**, 387.
[22] *Ann. Reports*, 1924, **21**, 91; 1925, **22**, 100; compare S. M. Neale, *J. Text. Inst.*, 1925, **16**, T363; **A.**, 1926, 241.
[23] H. Pringsheim and J. Leibowitz, *Ber.*, 1925, **58**, 2808; **A.**, 1926, 275.
[24] *Ber.*, 1926, **59**, 3019.

mixed with a methylated trisaccharide.[25] An analysis of the mixture agreed with a 70% content of the former and 30% of the latter, as did also molecular-weight determinations. Hydrolysis of this mixture of products yielded 2 : 3 : 6-trimethyl glucose (84%) and also 2 : 3 : 4 : 6-tetramethyl glucose (7%). Evidence of the presence of an acetylated disaccharide other than cellobiose was also recorded. The authors conclude from these results that support is given to the application of the poly(1 : 4-anhydroglucose) structure to cellulose, and they modify their earlier suggestion of four possible constitutional formulæ by the elimination of identical representations and by the introduction of amylene-oxide rings into the glucose residues. The direct evidence available is to some extent obscured by the non-homogeneity of the original acetates.

Another series of investigations [26] on cellulose indicates the ease of methylation which is secured by employing cellulose regenerated from viscose or cellulose acetate. Also by utilising depolymerised cellulose, obtained as hydrocellulose from viscose staple fibre, nine methylations with methyl sulphate sufficed to introduce a complete complement of methyl groups corresponding to trimethyl cellulose. The same result is obtained when dimethyl cellulose prepared from viscose cellulose is first acetylated and then twice methylated. The most striking result appeared to be that obtained by methylating cellulose triacetate from cotton linters, inasmuch as a trimethyl cellulose was isolated after only six methylations. This product is soluble in acetic acid, and almost completely dissolves in cold water. Determinations of molecular weight give 800 as the lowest value for a hydrocellulose.

Inulin.

Acetylation of inulin in presence of pyridine at temperatures between 20° and 60° leads to an 80% yield of inulin hexa-acetate, m. p. 135°. Molecular-weight determinations indicate that this product is hexa-acetyl difructose anhydride,[27] and the view that inulin is built up from the unit $C_{12}H_{20}O_{10}$ is supported by these results. Hydrolysis of the hexa-acetyl derivative regenerates inulin, which in turn gives back the hexa-acetyl difructose anhydride on reacetylation. Inulin has been dissolved in liquid ammonia, and it is remarkable that from this solution it can be recovered unchanged.

[25] J. C. Irvine and G. J. Robertson, *J.*, 1926, 1488; **A.**, 823.

[26] E. Heuser and N. Heimer, *Cellulosechem.*, 1925, **6**, 101; **A.**, 1926, 502; H. le B. Gray, *Ind. Eng. Chem.*, 1926, **18**, 811; **A.**, 1026.

[27] M. Bergmann and E. Knehe, *Annalen*, 1926, **449**, 302; **A.**, 1230; M. Bergmann, *Ber.*, 1926, **59**, 2079.

Acids, Fats, and Waxes.

Ultra-violet light decomposes a boiling solution of formic acid with the production of hydrogen and carbon dioxide and also into water and carbon monoxide.[1] The intermediate formation of methyl alcohol or formaldehyde has been disputed, but it is established that if the formic acid is sufficiently concentrated, the greater part of the nascent hydrogen and carbon monoxide reacts with the formic acid to give formaldehyde, etc.[1a] The catalytic decomposition of formic acid in presence of metals is largely influenced by the dispersivity of the latter, and falls rapidly as the catalyst becomes aggregated. Oxalic acid undergoes electrolytic reduction to glyoxylic acid in solutions containing 2% of sulphuric acid. By continuous addition of oxalic and sulphuric acids during the progress of the electrolysis a solution containing more than 12% of glyoxylic acid has been prepared. A detailed study[2] of this process is communicated, including the methods of isolation of the product. Pyruvic acid may be obtained[3] in yields of 90% by the oxidation of methylglyoxal with bromine water. Propiolic acid is conveniently prepared by the action of carbon dioxide on sodium acetylide,[4] and the pure crystalline acid obtained by this method can be kept indefinitely without polymerisation occurring. Propiolic anhydride is readily obtained from the sodium salt by the agency of thionyl chloride. By employing the same procedure, and using disodium acetylide, acetylenedicarboxylic acid is obtained.

Oxidation of the sodium derivative of acetoacetic acid or its ethyl ester by means of hydrogen peroxide yields mainly α-hydroxyacetoacetic acid or its corresponding enol form.[5] This acid gradually passes into acetylcarbinol by loss of carbon dioxide, and by subsidiary reactions acetonylacetone, glyoxylic acid, and other products are formed. The possibility of the formation of carbohydrate in the living organism from acetoacetic acid is discussed on the basis of these results. The addition of ethyl diethoxyacetate in successive portions to sodium ethoxide in ether gives rise to the ester enolate, which decomposes in presence of ice, yielding diethoxymethylene.[6] The same product may also be obtained by converting ethyl formate similarly into the sodium derivative of hydroxyethoxymethylene, C(ONa)OEt, followed by chlorination

[1] E. Müller and H. Hentschel, *Ber.*, 1926, **59**, 1854; **A.**, 1124.
[1a] A. J. Allmand and L. Reeve, *J.*, 1926, 2853.
[2] W. Mohrschulz, *Z. Elektrochem.*, 1926, **32**, 434; **A.**, 1110.
[3] C. Neuberg and G. Gorr, *Biochem. Z.*, 1926, **166**, 442; **A.**, 272.
[4] F. Straus and W. Voss, *Ber.*, 1926, **59**, 1681; **A.**, 1124.
[5] P. W. Clutterbuck and H. S. Raper, *Biochem. J.*, 1926, **20**, 59; **A.**, 427.
[6] H. Scheibler, *Ber.*, 1926, **59**, 1022; **A.**, 711.

with phosphoryl chloride and treatment with sodium ethoxide. The products appear to be true derivatives of carbon monoxide and compounds of bivalent carbon.

Thallous salts of organic acids have been prepared by titration with thallous hydroxide solution, and many of these crystalline salts are described. Their utility in synthetic work is illustrated,[7] and they possess obvious advantages over the silver salts as a means of preparing the corresponding esters by digestion with alkyl halides. Small quantities can easily be manipulated and traces of the acids readily recognised owing to the facility with which esterification proceeds. Palmitic, stearic, and oleic acids give thallous salts, m. p.'s 115°, 119°, and 78—82°, respectively, and these show double m. p.'s and appear to be anisotropic liquids between these points. Tartaric acid gives a tetrathallium derivative, losing, however, two of the metallic radicals by the agency of carbon dioxide.

The two stereoisomeric hydroxystearic acids (m. p. 95° and 132°) may be prepared by the oxidation of oleic acid and elaïdic acid, respectively, by concentrated hydrogen peroxide in acetic acid or acetone solution.[8] Under the same conditions, methyl oleate and elaïdate give the corresponding esters of the two isomerides. If the oxidation be conducted, however, under alkaline conditions the dihydroxystearic acid having the higher m. p. is obtained from oleic acid, indicating a transformation of the geometric isomerides.

By an application of the method described in the last Report (p. 80), ι-ketostearic acid has been synthesised.[9] Reference to the freezing-point curve for mixtures of ι-ketostearic and κ-ketostearic acids indicates that the product obtained by treating stearolic acid with sulphuric acid and then with water consists of a mixture of these two acids.

In addition to the above, the following have also been prepared by the same authors : δ-ketomyristic acid and its oxime, κ-ketononadecoic acid and its amide, and κ-ketobehenic acid and its amide.

Partial hydrogenation of stearolic acid in presence of nickel has given rise to oleic acid, and by the same procedure behenolic acid yields erucic acid.[10] The corresponding products obtained by reduction with zinc and acetic acid are elaïdic and brassidic acids. It is argued on thermochemical grounds that no secondary changes are involved in the former of these methods of reduction, and

[7] G. H. Christie and R. C. Menzies, *J.*, 1925, **127**, 2369; **A.**, 1926, 55; C. M. Fear and R. C. Menzies, *J.*, 1926, 937; **A.**, 604.

[8] T. P. Hilditch, *J.*, 1926, 1828; **A.**, 938.

[9] G. M. Robinson and R. Robinson, *ibid.*, p. 2204; **A.**, 1024.

[10] A. González, *Anal. Fis. Quím.*, 1926, **24**, 156; **A.**, 712.

therefore that oleic and erucic acids have the *cis*-configuration whilst elaïdic and brassidic have the *trans*.

Incomplete hydrogenation of castor oil in presence of a nickel catalyst at 80° leads to a convenient process [11] for the preparation of ethyl λ-hydroxystearate, m. p. 51°. After reduction, the mixed glycerides are converted into the corresponding ethyl esters and recrystallised. Either by heating ethyl λ-hydroxystearate with β-naphthalenesulphonic acid at 220° or by treating the free acid with thionyl chloride, and then with ethyl alcohol, this is transformed into the isomeric ethyl Δ^{λ}-octadecenoate, and from this both forms of the related acid are obtained, the elaïdic type having m. p. about 40°, and the oleic type m. p. about 10°. The latter is isomerised partly to the elaïdic type by nitric acid at 25° in presence of mercury. Ethyl $\lambda\mu$-dibromo-octadecanoate readily loses 1 molecule of hydrogen bromide to give ethyl bromo-Δ^{λ}-octadecenoate, but under more drastic conditions, using alcoholic potassium hydroxide, Δ^{λ}-octadecinenoic acid, m. p. 34·2°, is produced. Oxidation of the acetylenic acid with alkaline permanganate leads to decane-$\alpha\kappa$-dicarboxylic, nonane-$\alpha\iota$-dicarboxylic, sebacic, and hexoic acids, whilst further successive oxidation with chromic acid gives hexoic, valeric, and decane-$\alpha\kappa$-dicarboxylic acids. It would thus appear that elimination of water from λ-hydroxystearic acid occurs exclusively to form the Δ^{λ}-unsaturated acid.

The acid, $C_{24}H_{46}O_2$, which is designated nervonic acid [12] and is obtained by hydrolysis of the cerebroside isolated from human brain, yields on reduction with hydrogen and colloidal palladium a saturated fatty acid, m. p. 85°. This is said to be identical with *n*-tetracosoic acid. The hydrolysis of certain cerebroside fractions gives rise to a new acid, $C_{24}H_{46}O_3$, which is probably an unsaturated hydroxy-acid.

From the crude arachidic acid prepared from arachis oil, a hexacosoic acid, $C_{26}H_{52}O_2$, of m. p. 79° has been isolated [13] and this is probably identical with cerotic acid from beeswax. The unsuspected presence of this acid explains the difficulties experienced in isolating lignoceric acid, $C_{24}H_{48}O_2$, and also the discrepancies observed as to its physical constants. The m. p. of the latter is given as 80·5—81°. An *X*-ray examination [14] of the hexacosoic acid confirms this observation.

Crystalline stearolactone [15] is formed as one of the products of

[11] A. Grün and W. Czerny, *Ber.*, 1926, **59**, 54; **A.**, 269; compare Thoms and Deckert, *A.*, 1921, i, 219.

[12] E. Klenk, *Z. physiol. Chem.*, 1926, **157**, 283, 291; **A.**, 1124.

[13] D. Holde and N. N. Godbole, *Ber.*, 1926, **59**, 36; **A.**, 268.

[14] G. T. Morgan and E. Holmes, *Nature*, 1926, **117**, 624; **A.**, 712.

[15] A. Blumenstock, *Monatsh.*, 1926, **46**, 333; **A.**, 597.

the action of zinc chloride on oleic acid, and also by sulphonation of pure oleic acid followed by distillation and fractional crystallisation.

Not only oleic acid, but also the unsaturated acid of linseed oil, is reduced by the action of a methyl-alcoholic solution of hydrazine on fats.[16] The products are first isolated as the hydrazides, and the free acids are obtained by heating these with sulphuric acid and benzaldehyde.

Polymethylenedicarboxylic acids containing 11—19 carbon atoms in the chain and designed for conversion into the corresponding ketones were prepared by methods [17] which clearly indicate their constitution. Thus nonane-$\alpha\iota$-diol, prepared by the reduction of azelaic ester by the action of sodium and alcohol, and also decane-$\alpha\kappa$-diol, were converted into the dibromides and thence, through the cyanides or by condensation with ethyl malonate, into the higher carboxylic acids. The esters of these were reduced to the corresponding glycols, which provided new materials for similar syntheses A variation of this method was also employed; thus the dibromo-compounds, through their magnesium derivatives, were condensed with monochlorodimethyl ether, yielding the dimethoxy-derivatives of hydrocarbons containing two more carbon atoms in the chain: $MgBr\cdot[CH_2]_n\cdot MgBr + 2CH_2Cl\cdot OMe \longrightarrow MeO\cdot[CH_2]_{n+2}\cdot OMe$. By the action of dry hydrogen bromide on the latter, the corresponding dibromo-derivatives were obtained.

The compounds isolated by these methods range from nonane- to heptadecane-dicarboxylic acids. The m. p.'s of the even-numbered dicarboxylic acids fall from the one acid to the next, whilst the m. p.'s in the odd-numbered series rise, so that the curves for the two series of m. p. tend to converge.

A second form of $\alpha\alpha'$-dibromosuberic acid has been isolated. Both varieties give, when boiled with aqueous sodium carbonate, $\alpha\alpha'$-dihydroxysuberic acid.[18] When ethyl $\alpha\alpha'$-dibromosuberate is digested with methyl-alcoholic potassium hydroxide, it yields the open-chain unsaturated acid, suberocolic acid, reduction of which yields two forms of dihydrosuberocolic acid. Other products of this treatment with alkali are *cyclo*hexene-1 : 2-dicarboxylic acid and $\alpha\alpha'$-dimethoxysuberic acid. Dimethoxyazelaic acid and dihydroxyazelaic acid in stereoisomeric forms were isolated by similar treatment of ethyl $\alpha\alpha'$-dibromoazelate. Synthetic waxes have been prepared [19] by heating mixtures of the higher acids and alcohols in iron vessels or in the presence of molten tin, the ester

[16] J. van Alphen, *Rec. trav. chim.*, 1925, **44**, 1064; **A.**, 1926, 46.

[17] P. Chuit, *Helv. Chim. Acta*, 1926, **9**, 264; **A.**, 499.

[18] F. R. Goss and C. K. Ingold, *J.*, 1926, 1471; **A.**, 820.

[19] A. Grün, E. Ullrich, and F. Krezil, *Z. angew. Chem.*, 1926, **39**, 421; **A.**, 596.

mixture so formed having the consistency, plasticity, and conchoidal fracture of most waxes. The pure alcohols also combine with the acid chlorides when heated in an atmosphere of carbon dioxide and give almost quantitative yields of wax esters. The following have *inter alia* been prepared: μ-tricosyl myristate, palmitate, and stearate, and the corresponding ε-heptacosyl, π-hentriacontyl, and σ-pentatriacontyl esters.

The complex process involved in the electrolysis of potassium acetate has again been the subject of inquiry,[20] and in a recent communication the "discharged ion" theory as originally proposed by Crum Brown and Walker is supported as against the "oxidation" theory. It has been shown that synthesis takes place in non-aqueous solutions to which the oxidation theory cannot be applied.

Optical Activity.

Of the views put forward respecting the spatial configuration of the ammonium salts, those deserving of more serious consideration assign to the four positive radicals attached to the nitrogen atom a disposition which is either tetrahedral or pyramidal, these being the only arrangements in which the valencies linking the nitrogen atom with these radicals can be represented as inter-equivalent. Whilst on general grounds the tetrahedral configuration of the ammonium salts must be regarded as the more probable, no direct experimental evidence had hitherto been obtained which enabled a definite decision to be made between this and the pyramidal configuration. W. H. Mills and E. H. Warren [1] have decided this important question by a successful resolution of 4-phenyl-4′-carbethoxybispiperidinium-1 : 1′-spiran bromide,

$$\left[\begin{matrix}\mathrm{H}\\ \mathrm{Ph}\end{matrix}\!>\!\mathrm{C}\!<\!\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}\!>\!\mathrm{N}\!<\!\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}\!>\!\mathrm{C}\!<\!\begin{matrix}\mathrm{H}\\ \mathrm{CO_2Et}\end{matrix}\right]\mathrm{Br},$$

in which a pyramidal configuration would be symmetrical whilst a tetrahedral distribution should exhibit dissymmetry. It must therefore be concluded that, in quaternary ammonium compounds, the four positive radicals are disposed tetrahedrally about the nitrogen atom, the fifth radical being attached as a negative ion. This conclusion is confirmed by the previous failure to resolve trimethylenetetrahydro*iso*quinolinium salts.[2] In the case of the amine oxides, Nabc(O), upon which further work is contributed [2a] by Meisenheimer and his colleagues, the double bond between oxygen

[20] D. A. Fairweather and O. J. Walker, *J.*, 1926, 3111.

[1] *J.*, 1925, **127**, 2507; **A.**, 1926, 178.

[2] H. O. Jones and J. G. H. Dunlop, *J.*, 1912, **101**, 1748.

[2a] J. Meisenheimer, H. Glawe, H. Greeske, A. Schorning, and E. Vieweg, *Annalen*, 1926, **449**, 188; **A.**, 1240.

and nitrogen is semi-polar, the oxygen atom both figuring as the fourth positive radical and taking the place of the negative ion of the ammonium salts. Wedekind [3] has found it impossible to effect a resolution of quaternary ammonium bases with a double linking at the nitrogen atom, both when the double linking is between nitrogen and carbon, as in CPh:NMePhI, and when it is situated between two nitrogen atoms in a ring, as in PhC$\begin{matrix}\diagup \\ \diagdown\end{matrix}$$\begin{matrix}\text{N}\cdot\text{NPh} \\ \text{N:NPhBr}\end{matrix}$.

Many writers, following Werner, had assumed that the salts of bivalent metals with β-diketones and similar substances were examples of 4-co-ordination compounds, and that they possessed, therefore, a tetrahedral configuration of which the metallic atom was the centre. Such structures should clearly give rise to the possibility of optical activity due to the normally bivalent metallic atom alone, just as is the case with the octahedral structures of corresponding derivatives of normally tervalent metallic atoms such as cobalt and iron. H. Burgess and T. M. Lowry [4] had demonstrated this probability by an examination of the mutarotation of beryllium benzoylcamphor; but their results were perhaps not decisive owing to the presence of additional optical activity due to carbon. Now, however, Mills and R. A. Gotts [5] have supplied further proof of the hypothesis by the resolution of the beryllium, copper, and zinc salts of a β-diketone itself free from molecular dissymmetry. They employed benzoylpyruvic acid, effecting the resolution of the metallic salt by coupling it with brucine or strychnine. Thus, in the case of beryllium, they obtained both the *d*- and the *l*-rotatory salt of the structure *

$$\text{HC}\begin{matrix}\diagup \\ \diagdown\end{matrix}\begin{matrix}\text{CPh}\cdot\text{O} \\ \text{C}\!-\!\text{O} \\ \text{CO}_2\text{Bruc.}\end{matrix}\!\!>\text{Be}<\!\!\begin{matrix}\text{O}\cdot\text{CPh} \\ \text{O}\!-\!\text{C} \\ \text{CO}_2\text{Bruc.}\end{matrix}\!\!\begin{matrix}\diagup \\ \diagdown\end{matrix}\text{CH}\ ,$$

these salts mutarotating in chloroform to the same (*d*) value. In addition, they were able to replace the brucine radical by the dimethylammonium radical, and to show that the salt still retained the optical activity due to the metallic atom, although this activity vanished after about ¼ hour in alcoholic solution.

These experiments seem to furnish positive evidence, not only of the tetrahedral disposition of the valencies of the normally bivalent metallic atom in its 4-co-ordinated state, but also of the existence

* In this formula (following Mills and Gotts), the nature of the bonds between beryllium and oxygen is left undefined.

[3] E. Wedekind, *Annalen*, 1925, **442**, 119; *A.*, 1925, i, 678.

[4] *J.*, 1924, **125**, 2081; *A.*, 1925, i, 46; see also I. J. Faulkner and T. M. Lowry, *J.*, 1925, **127**, 1080; *A.*, 1925, ii, 632.

[5] *J.*, 1926, 3121.

of a real linking between the metallic atom and the carbonyl oxygen atom of the β-diketone. It will not be forgotten that the metallic derivatives of β-diketones are still sometimes represented as organo-metallic compounds in which the metal is linked to the inter-ketonic carbon atom. In the case of silver acetylacetone, for example, there is some evidence, although indecisive, in favour of the existence of both *O*-Ag and *C*-Ag salts, since alkyl substitution gives a mixture of the *O*-alkyl- and *C*-alkyl-acetylacetones. If such were the case with the benzoylpyruvic acid salts of the bivalent metals studied, salt formation would be accompanied by the development in each case of two similar dissymmetric carbon atoms. Current theory, however, is opposed to such a conception of the metallic salts of β-diketones, particularly in the case of a metal like copper. A resolution of the salt of a *symmetrical* β-diketone with a tervalent metal (*e.g.*, a ferric salt) would supply decisive evidence for the more widely accepted view; whilst an answer to the question as to whether or not a copper salt of a symmetrical β-diketone is resolvable would throw light upon the equivalence or otherwise of the linkings between the metal and the two oxygen atoms of the β-diketone.

In this connexion it may be remarked that I. Lifschitz [6] has claimed the preparation, from *d*-alanine and cobaltic hydroxide, of each of the salts *d*-[Co-*d*-alanine$_3$] and *l*-[Co-*d*-alanine$_3$], in which the cobalt atom exhibits octahedral dissymmetry although it is not associated with atoms or groups in the outer co-ordination sphere.

With regard to the distribution of the groups about the copper atom in its 4-co-ordinated compounds, reference [7] may be made to N. Schlesinger's copper salts of *bis*-imino-acids, which exist in reddish-violet and blue varieties. In this instance, *cis*- and *trans*-isomerism is held to be present, in which case the arrangement of the groups about the copper atom would be planar—unless tetrahedral nitrogen were assumed [7a] to be present.

R. Charonnat has succeeded in resolving [8] potassium ruthenonitrosopyridinodioxalate, [Ru(NO)(C_5H_5N)(C_2O_4)$_2$]K, by double decomposition with quinine hydrochloride.

The possibility that corresponding compounds of nitrogen, phosphorus, and arsenic might possess similar stereochemical configurations has led to many attempts to resolve arsonium compounds, but until recently the only positive result was that recorded by G. J. Burrows and E. E. Turner,[9] who obtained a solution of

[6] *Proc. K. Akad. Wetensch. Amsterdam*, 1924, **27**, 721; *A.*, 1925, i, 522.
[7] *Ber.*, 1925, **58**, 1877; *A.*, 1925, i, 1249.
[7a] H. Reihlen, *Z. anorg. Chem.*, 1926, **151**, 71; **A.**, 457.
[8] *Compt. rend.*, 1924, **178**, 1423; *A.*, 1925, ii, 586.
[9] *J.*, 1921, **119**, 426.

phenyl-α-naphthylbenzylmethylarsonium iodide (I) which showed a small dextrorotation. The preparation of the optically pure enantiomorphous modifications of *p*-carboxyphenylmethylethylarsine sulphide (II), $[M]^{20°}_{5461}$ +60° and −59°, by W. H. Mills and R. Raper,[10] definitely proves that arsenic can function as a centre of dissymmetry.

(I.) $\left[\begin{matrix}C_6H_5\\C_{10}H_7\end{matrix}\!\!>\!As\!<\!\!\begin{matrix}CH_3\\C_7H_7\end{matrix}\right]I$ $\qquad$ $\begin{matrix}CO_2H\cdot C_6H_4\\C_2H_5\end{matrix}\!\!>\!As\!<\!\!\begin{matrix}S\\CH_3\end{matrix}$ (II.)

The grouping $R_1R_2R_3As{:}S$ forms a chemically indifferent complex unlike the tertiary amine and phosphine oxides resolved by Meisenheimer, which are basic substances. The salt-forming properties of this arsenic compound are derived from the substituent carboxyl group and the arsenic atom is thereby left as far as possible undisturbed by the process of salt formation and decomposition involved in the resolution experiments. Here again it seems probable that the four radicals are tetrahedrally distributed with respect to the arsenic atom, and that, as in the amine and phosphine oxides, a semipolar double bond is present (in this case, between arsenic and sulphur).

Of much interest, also, is the resolution [11] of a co-ordinated arsenic compound which contains, apparently, arsenic of octahedral configuration and is possessed of high rotatory power. The substance is tripyrocatechylarsenic acid, discovered by R. F. Weinland and J. Heinzler,[12] to which has been ascribed [13] the formula

$$\left[(C_6H_4O_2)_2{\equiv}As\!<\!\!\begin{matrix}H_2O\\O\cdot C_6H_4\cdot O\end{matrix}\right]H.$$

Although the discoverers of optical activity in this compound favour the above formula, the possibility that the compound is correctly represented as having the three pyrocatechyl radicals octahedrally distributed around the central arsenic atom should not be overlooked,[14] in spite of the tenacity with which a molecule of water is retained in the acid and in all its salts.

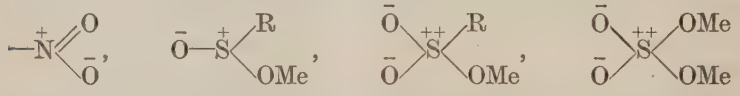
The case of arsenic appears to afford the first recorded instance of an element which gives rise to dissymmetry of both tetrahedral and octahedral type.

A compound of 4-co-ordinated boron, disalicylatoboric acid,

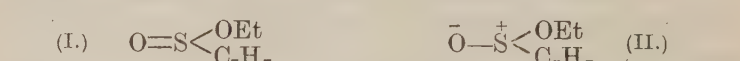
[10] *J.*, 1925, **127**, 2479; **A.**, 1926, 77.
[11] A. Rosenheim and W. Plato, *Ber.*, 1925, **58**, 2000; *A.*, 1925, i, 1412.
[12] *Ber.*, 1919, **52**, 1316; 1920, **53**, 1358; *A.*, 1919, i, 442; 1920, i, 778.
[13] H. Reihlen, A. Sapper, and G. A. Kall, *Z. anorg. Chem.*, 1925, **144**, 218; *A.*, 1925, i, 912.
[14] Compare W. H. Mills and R. A. Gotts, *loc. cit.*

$[B(O_2C{\cdot}C_6H_4{\cdot}O)_2]H$, in which boron possesses a tetrahedral configuration, has been resolved [15] by means of its strychnine salt.

The existence of the semipolar double bond, postulated by Lowry [16] some three years ago, has now been established by two independent experimental methods, depending respectively on the study of molecular volumes and on the detection of molecular dissymmetry. By making use of the function $\gamma^{1/4}M/(D-d)$ (where γ = surface tension, M = mol. wt., D = density of liquid, d = density of vapour), S. Sugden [17] compares molecular volumes at equal surface tensions. The value of this function, known as the parachor, is increased by 23 units by each non-polar double bond, whatever the atoms which it joins, *e.g.*, in >C=O, >C=C<, >C=N–, –N=O, but the semipolar double bonds in the systems >SO, ⩾NO, and ⩾PO produce a minute decrement of molecular volume.[18] In this way, the nitro-group was shown to contain only one non-polar double bond, whilst the sulphinates, sulphonates, and sulphates do not contain any.



The importance of these observations is seen in the discovery of optical activity in compounds which have only three groups attached to a central sulphur atom. The demonstration by H. Phillips [19] that the sulphinates can be obtained in optically active forms, as in the case of ethyl *p*-toluenesulphinate, provides substantial experimental evidence that the constitution of this ester is not accurately represented by the usually accepted formula (I).



If the oxygen and the sulphur were united by a symmetrical non-polar double bond, the compound would, on the basis of the older space formulæ, be obviously symmetrical. This formula (I) is also in conflict with the postulates of the newer theories of valency, since the presence of a non-polar double bond between the sulphur and the sulphoxyl oxygen atom would create a surplus of valency

[15] J. Böeseken and J. Meulenhoff, *Proc. K. Akad. Wetensch. Amsterdam*, 1924, **27**, 174; *A.*, 1924, i, 776; J. Meulenhoff, *Z. anorg. Chem.*, 1925, **142**, 373; *A.*, 1925, i, 920.

[16] *J.*, 1923, **123**, 822.

[17] *J.*, 1924, **125**, 1177; *A.*, 1924, ii, 662.

[18] S. Sugden, J. B. Reed, and H. Wilkins, *J.*, 1925, **127**, 1525; *A.*, 1925, ii, 936.

[19] *Ibid.*, p. 2552; **A.**, 1926, 159.

electrons (10 instead of 8) in the valency shell of the sulphur atom. Since the determination of the molecular parachor of ethyl *dl*-*p*-toluenesulphinate revealed that the sulphur and the oxygen were linked by a semipolar double bond, formula (II) was adopted as more accurately representing the constitution of this ester. The newly-discovered dissymmetric ester molecule can therefore be considered as having a tetrahedral configuration in which the apex is occupied by the positively-charged sulphur atom, two other corners by the *p*-tolyl and the ethoxy-group, respectively, whilst the remaining corner is occupied by the oxygen atom, united to sulphur by a semipolar double bond. From such considerations, P. W. B. Harrison, J. Kenyon, and H. Phillips [20] were led to revise the accepted formula (III) for the sulphoxides and to suggest a new formulation (IV) which carried with it the implication that mixed sulphoxides should exist in an optically active state.

(III.) $O{=}S{<}^{R}_{R'}$ $\bar{O}{-}\overset{+}{S}{<}^{R}_{R'}$ (IV.)

4′-Amino-4-methyldiphenyl sulphoxide (V) and *m*-carboxyphenyl methyl sulphoxide (VI) were prepared and resolved into enantiomorphous modifications.

(V.) $\bar{O}{-}\overset{+}{S}{<}^{C_6H_4\cdot NH_2}_{C_6H_4Me}$ $\bar{O}{-}\overset{+}{S}{<}^{C_6H_4\cdot CO_2H}_{CH_3}$ (VI.)

It is to be noted that the oxidation of the active sulphinates and sulphoxides to sulphonates and sulphones, respectively, results in disappearance of the optical activity.

It may now be considered as definitely established that the fourth valency of quadrivalent sulphur differs from the three other valencies. This experimental fact is in agreement with the electronic theories of valency, according to which sulphur, when quadrivalent, is linked to other atoms by three co-valencies and one electrovalency, a conclusion which was foreseen by Werner.[21] Here is a further example of the general rule, already illustrated in the case of Werner's theory of co-ordination, that each new development of the theory of valency has been accompanied by and has received its final sanction from the discovery of a new kind of optical activity.[22]

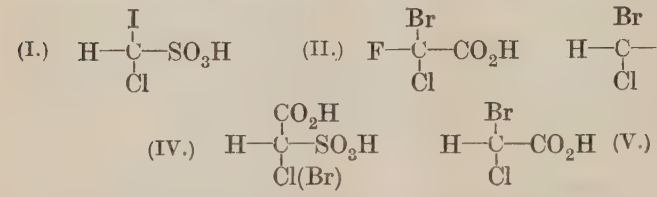
An interesting procedure for the recognition and resolution of an externally compensated conglomerate of *d*- and *l*-forms is described [23] by G. T. Morgan, W. J. Hickinbottom, and T. V. Barker in their

[20] *J.*, 1926, 2079; **A.**, 1031.
[21] "Lehrbuch der Stereochemie," 1904, p. 317.
[22] T. M. Lowry, *Nature* (Suppt.), May, 1926, p. 40.
[23] *Proc. Roy. Soc.*, 1926, [*A*], **110**, 502; **A.**, 503.

paper on the stereoisomeric $\beta\gamma$-diamino-*n*-butanes. Their method, which may be applied to all substances having definite melting points, has been successfully used for the recognition of ψ-racemoids and racemoids.

The Resolution of Simple Types of Carbon Compounds.

Some interesting resolutions of compounds containing only one or two carbon atoms have recently been demonstrated. It will be recalled that chloroiodomethanesulphonic acid (I) is relatively optically stable (Pope and Read), whereas fluorochlorobromoacetic



acid (II) becomes racemised immediately on liberation from its active alkaloidal salts (Swarts). It has now been shown [24] by J. Read and A. M. McMath that chlorobromomethanesulphonic acid (III) is at the same time more active and less optically stable than the corresponding acid (I) in which iodine replaces the bromine atom. The bromo-acid (III) was resolved by the use of active hydroxyhydrindamine, the resolution being accompanied, in acetone solution, by the deposition of the crystalline *l*-A, *l*-B salt (when the *l*-base was used), followed by that of crystals of the *dl*-A, *l*-B salt. The latter salt was progressively transformed, by further crystallisation from acetone, into the *l*-A, *l*-B salt, thus exhibiting a behaviour similar to that observed by Pope and Peachey [25] during the resolution of methylethylpropylstannonium iodide by means of *d*-camphor-π-sulphonic acid. The resolution of chloro- and bromo-sulphoacetic acids (IV), by Backer, Burgers, and Mook,[26] and subsequently (in the case of the chloro-acid) by Read and McMath,[27] and of chlorobromoacetic acid (V) by the latter authors,[28] affords further instances of optical activity amongst simple types of compounds.

The period under review has seen the disappearance for all practical purposes of the Kaufler formula, in accordance with which the rings in benzidine and other derivatives of diphenyl, and

[24] *J.*, 1925, **127**, 1572; *A.*, 1925, i, 1126.

[25] *P.*, 1900, **16**, 42, 116.

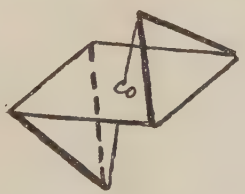
[26] H. J. Backer and W. G. Burgers, *J.*, 1925, **127**, 233; *A.*, 1925, i, 359; *Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 64; *A.*, 1925, i, 631; H. J. Backer and H. W. Mook, *ibid.*, p. 65; *A.*, 1925, i, 632.

[27] *J.*, 1926, 2192; **A.**, 1025.

[28] *Ibid.*, p. 2183; **A.**, 1024.

even in naphthalene and fluorene, were regarded as situated in inclined planes (see p. 120). There remains, however, the undoubted resolvability of certain ortho-substituted diphenic acids; and this can only be accounted for in a satisfactory manner by assuming that the rings, while co-axial, are not co-planar. This hypothesis, unlike that of Kaufler, accords with the stereochemistry of the Kekulé benzene ring, in which the six bonds to hydrogen or to substituent atoms are situated in the plane of the ring.

Pope and Mann have shown [38] that $\alpha\beta\gamma$-triaminopropane, $CH_2(NH_2)\cdot CH(NH_2)\cdot CH_2(NH_2)$, is capable of forming co-ordination compounds with cobalt and rhodium in which the triamine occupies three co-ordination positions. The cobalt salt is represented by the formula $[Co\ ptn_2]Cl_3$, where " ptn " denotes the triaminopropane molecule. It will be seen that ptn replaces $3NH_3$ in hexamminocobaltic chloride, $[Co(NH_3)_6]Cl_3$, the molecule of the triamine being bent at an angle of 60° about the central carbon atom, so that the organic chain is wrapped about three corners of the octahedron. Of three possible arrangements of this kind the authors consider the irresolvable form



to be the most probable (the thick lines represent the ptn molecule); but apparently a labile resolvable modification has also a transient existence, since the authors have detected fugitive optical activity in the chloride.

G. T. Morgan and J. D. M. Smith report [39] that Combes's ethylenediaminobisacetylacetone is capable of occupying four co-ordination positions around cobalt. The compound thus obtained was resolvable, and two optically active stereochemical modifications were isolated. In this case also the optical activity was fugitive.

The question as to whether the adsorption of dyes by animal and vegetable fibres is a physical or a chemical process is still unsettled. Porter and his collaborators recorded [40] that one of the

[38] *Compt. rend.*, 1924, **178**, 2085; *Proc. Roy. Soc.*, 1925, [*A*], **107**, 80; *A.*, 1925, i, 373; *J.*, 1926, 2675. Compare also *J.*, 1926, 482, 489.

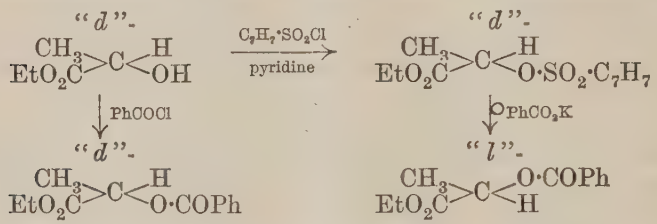
[39] *J.*, 1925, **127**, 2030; *A.*, 1925, i, 1457.

[40] C. W. Porter and C. T. Hirst, *J. Amer. Chem. Soc.*, 1919, **41**, 1264; *A.*, 1919, i, 558; C. W. Porter and H. K. Ihrig, *ibid.*, 1923, **45**, 1990; *A.*, 1923, i, 1027.

optically active isomerides of a dissymmetric azo-dye was selectively adsorbed by wool and silk, and G. T. Morgan and D. G. Skinner obtained [41] similar results. These results, however, have not been confirmed by the recent work [42] of W. R. Brode and R. Adams.

The Walden Inversion.

An interesting aspect of the Walden inversion is illuminated by a paper [44] from J. Kenyon, H. Phillips, and H. G. Turley, in which an account is given of the transformation of ethyl "*d*"-lactate to its fully active benzoyl derivative by either of two routes, one of which leads to the "*d*"- and the other to the "*l*"-benzoyl derivative :



Here it is possible to decide definitely at what stage the complete inversion occurs, because atoms of the *same* elements are attached to the dissymmetric carbon atom before and after transformation. The authors trace an analogy in the behaviour of the *p*-toluenesulphonoxy-radical and the halogen atom in such reactions of similar α-substituted esters, and reach conclusions regarding relative configurations which are opposed in some respects to those expressed [45] by G. W. Clough as a result of his studies of the effects of temperature, concentration, and the presence of inorganic salts on the rotatory powers of related active compounds.

Clough's important conclusion, that the naturally occurring amino-acids possess the same relative configurations (*loc. cit.*, p. 539), is now confirmed,[46] and is extended to include the simpler alkaloids.

A. McKenzie, R. Roger and G. O. Wills have observed [47] that when *l*-β-amino-αα-diphenyl-*n*-propyl alcohol (I) is treated with nitrous acid, it is changed into the highly active *d*-ketone (III), the asymmetric carbon atom (asterisk) retaining its activity, even

[41] *J.*, 1925, **127**, 1731; *A.*, 1925, i, 1191.

[42] *J. Amer. Chem. Soc.*, 1926, **48**, 2193, 2202; **A.**, 1031.

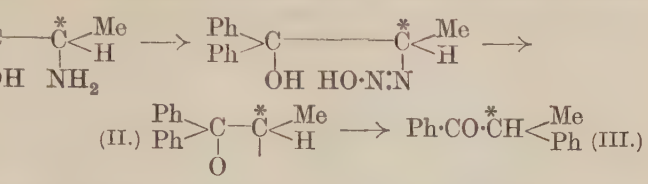
[44] *J.*, 1925, **127**, 399; compare also H. Phillips, *J.*, 1923, **123**, 44.

[45] *J.*, 1918, **113**, 526; compare also *J.*, 1926, 1674.

[46] P. Karrer, K. Escher, and R. Widmer, *Helv. Chim. Acta*, 1926, **9**, 301; **A.**, 505.

[47] *J.*, 1926, 779; **A.**, 610.

although in the intermediate stage (II) it is associated with only three groups. It is not known whether a Walden inversion accom-



panies the change. The authors offer the tentative suggestion that the asymmetry is temporarily retained owing to the presence of an electric charge on the carbon atom, although they leave undefined the nature and origin of the charge. As they mention, a similar but more definite hypothesis has already been advanced [48] by E. Biilmann in connexion with the action of silver ions upon α-bromopropionic acid, and more recently B. Holmberg [49] has utilised the same conception in connexion with the changes undergone by chlorosuccinamic acid. This hypothesis of dissymmetric carbon associated with three dissimilar radicals and a positive charge is paralleled by that advanced by Kenyon, Phillips, and Turley for the active sulphoxides,[50] and is in accordance both with the conceptions of Werner and with Baeyer's hypothesis of carbonium salts. In the case under discussion, it would seem possible to regard the unsaturated carbon atom (formula II) as carrying a positive charge, the neighbouring unsaturated oxygen carrying a negative charge, these charges resulting from the ionisation of a carbon to oxygen linking in the intermediate oxide :

If then the change to (III) occurred by the migration of a phenyl radical carrying an electron (*i.e.* of a phenyl anion), the charges would automatically disappear during the transformation, as, in fact, they do.

Optically active ketones of the foregoing type are very readily racemised by a trace of alcoholic alkali, and McKenzie, Roger, and Wills suggest that loss of activity is brought about by enolisation *after* formation of an additive complex with potassium ethoxide, the tendency towards enolisation being practically nil in the ketone alone.

[48] *Annalen*, 1912, **388**, 330; *A.*, 1912, i, 420.
[49] *Ber.*, 1926, **59**, 1569; **A.**, 937.
[50] *Loc. cit.*

In continuation of the work of Senter upon the influence of the solvent in displacements involving the optically active carbon atom, it has been found [51] that the bromo-acid produced by the action of hydrogen bromide upon a given active β-hydroxy-β-phenylpropionic acid in various solvents has always the same sign; and that the same is true of the conversion of the active β-bromo-acid into the β-hydroxy-amide by means of ammonia in various solvents. The phenomenon of solvent inversion has, therefore, been demonstrated so far only in the case of phenylhalogenoacetic acids.

W. N. HAWORTH.

PART II. HOMOCYCLIC DIVISION.

Large Carbon Rings.

INVESTIGATIONS of outstanding interest have been published during the year by Ruzicka and his collaborators, who have prepared a series of homologous ring ketones, $(CH_2)_n{>}CO$, extending to the ketone with a ring of 18 carbon atoms. Since no pure monocyclic compound having a carbon ring of more than 8 atoms has previously been obtained, this work constitutes a most notable advance in our knowledge of homocyclic types.

The preparation of ring ketones by the distillation of the calcium salts of the normal-chain dicarboxylic acids has in the past been limited to *cyclo*pentanone, *cyclo*hexanone and *cyclo*heptanone (suberone), which can be obtained in upwards of 30% yields from adipic, pimelic, and suberic acids, respectively. H. Mayer and G. K. H. Derlon [1] believed that they had prepared *cyclo*octanone from calcium azelate, but it is now clear [2] that their product contained *cyclo*hexanone, methyl heptyl ketone, and an unidentified ketone, in addition to *cyclo*octanone. The first satisfactory synthesis of a *cyclo*octane derivative was carried out by O. Wallach,[3] who prepared *cyclo*octanone by oxidation of the crude *cyclo*octanol obtained by the action of nitrous acid on suberylmethylamine (Demjanov's reaction [4]). This work, together with that of Ciamician and Silber and of Willstätter on the degradation of the alkaloid

[51] G. Senter and A. M. Ward, *J.*, 1924, **125**, 2137; *A.*, 1925, i, 31; *J.*, 1925, **127**, 1847; *A.*, 1925, i, 1128.

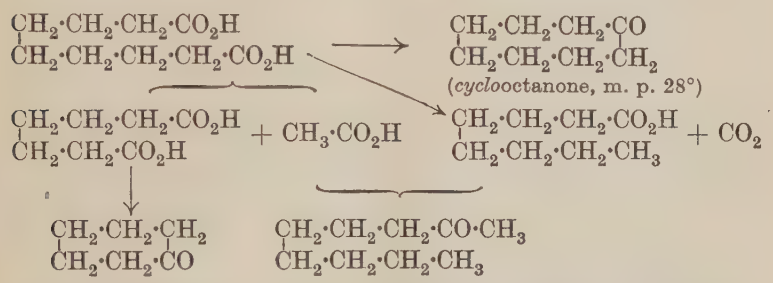
[1] *Annalen*, 1893, **275**, 363; *A.*, 1893, i, 557; *Ber.*, 1898, **31**, 1957; *A.*, 1898, i, 638.

[2] L. Ruzicka and W. Brugger, *Helv. Chim. Acta*, 1926, **9**, 339; **A.**, 611.

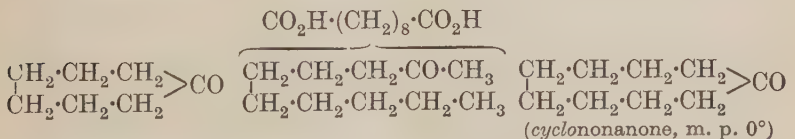
[3] *Annalen*, 1907, **353**, 328; *A.*, 1907, i, 602.

[4] N. J. Demjanov, *J. Russ. Phys. Chem. Soc.*, 1904, **36**, 166; *A.*, 1904, i, 410.

ψ-pelletierine, represents the approximate sum of our previous knowledge of *cyclo*octane and its derivatives. Ruzicka and Brugger have now shown [5] that 5% of pure *cyclo*octanone can be obtained from calcium azelate, and 10% from cerium azelate; their main discovery, however, is the fact that the use of the thorium salt increases the yield to 25%, thus rendering *cyclo*octanone for the first time a readily accessible material for the preparation of *cyclo*-octane derivatives. The identified by-products which arise during the distillations of these salts are those which would be formed if a part of the azelate were to undergo oxidative fission to a pimelate and an acetate, whilst another part lost a carboxyl group as carbon dioxide :



As R. Willstätter and T. Kametaka suspected,[6] the ketone obtained by distillation of calcium sebacate [7] is a mixture,[8] but pure *cyclo*nonanone may be obtained [9] by distilling thorium sebacate. The yield is only 1·5% and the by-products are suberone, methyl octyl ketone, and an unidentified higher ketone, corresponding, therefore, with the by-products accompanying *cyclo*octanone from thorium azelate :



The reaction is therefore unsatisfactory as a starting point for the preparation of *cyclo*nonane derivatives, but Ruzicka and Brugger [10] have applied a modification of the Demjanov process to *cyclo*octanone

[5] *Loc. cit.*

[6] *Ber.*, 1907, **40**, 3876; *A.*, 1907, i, 936. Compare R. Willstätter and Bruce, *ibid.*, p. 3980; *A.*, 1907, i, 1018.

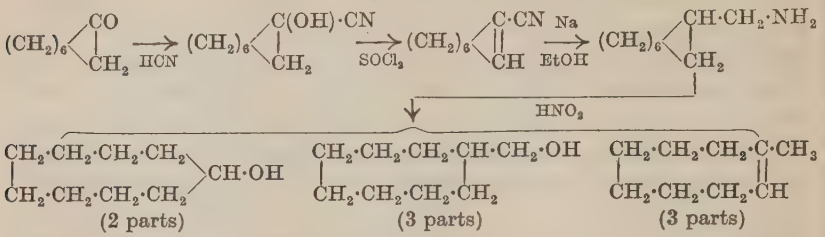
[7] N. Zelinsky, *ibid.*, p. 3277; *A.*, 1907, i, 780.

[8] L. Ruzicka and W. Brugger, *Helv. Chim. Acta*, 1926, **9**, 389; **A.**, 726.

[9] *Loc. cit.*

[10] *Ibid.*, p. 399; **A.**, 727.

with results which appear to form the basis of a feasible preparative method :



The *cyclo*nonanol is easily separated and can be smoothly oxidised to the *cyclic* ketone.

The higher ketones,[11] from C_{10} to C_{18}, were obtained by vacuum distillation of the thorium salts of the long normal-chain $\alpha\omega$-dicarboxylic acids.[12] The ketones were separated from the crude distillates in the form of semicarbazones, from which they were afterwards regenerated, and their structures were established by oxidation to the corresponding polymethylene-$\alpha\omega$-dicarboxylic acids. The yields of the ketones passed through a minimum (0·1—0·2%) at *cyclo*decanone and thereafter slowly rose with the increasing number of carbon atoms.

The ketones from *cyclo*dodecanone to *cyclo*octadecanone are solids at the ordinary temperature :

No. of C atoms in ring ...	10	11	12	13	14	15	16	17	18
M. p. of cyclic ketone ...	?	?	59°	32°	52°	63°	56°	63°	71°

As the molecular weight of the ketone increases, its odour changes; *cyclo*decanone, *cyclo*undecanone and *cyclo*dodecanone have the odour of camphor; the odour of *cyclo*terdecanone faintly resembles that of cedarwood, and in the ascending members of the series (C_{14} to C_{18}) the odour of cedarwood becomes increasingly apparent when the vapours are in high concentration. At greater dilutions, however, the predominant odour of *cyclo*tetradecanone and especially of *cyclo*pentadecanone is that of musk, whilst the odours of the highest members, *cyclo*hexa-, *cyclo*hepta-, and *cyclo*octa-decanone, under similar conditions, resemble that of civet.

*cyclo*Pentadecanone is now being manufactured, under the trade name " exaltone," as an artificial substitute for musk.

Stability of Large Carbon Rings.—A striking discovery, which is, however, in complete agreement with the Sachse-Mohr theory of

[11] L. Ruzicka, M. Stoll, and H. Schinz, *Helv. Chim. Acta*, 1926, **9**, 249; **A.**, 615.

[12] This vol., p. 101.

strainless rings,[13] is that these large rings, once formed, are just as stable as 5- and 6-membered rings.[14] The cyclic ketones from suberone to *cyclo*octadecanone underwent no change (except a small amount of charring and polymerisation) when heated with concentrated hydrochloric acid at 180—200°; certainly degradation to smaller molecules did not occur, and there was no evidence of any ring-fission or isomeric change. *cyclo*Heptadecanone was passed over thoria at 400—420° and recovered unaltered. *cyclo*-Pentadecane and *cyclo*heptadecane, two well-defined, crystalline hydrocarbons, m. p.'s 61° and 65°, which were prepared by reduction of the semicarbazones of the corresponding ring ketones, were recovered completely unchanged after heating with phosphorus and fuming hydriodic acid at 250°. It is pointed out [15] that according to the elementary strain theory a 7-ring is comparable with a 4-ring and a 17-ring with a 3-ring.

No. of carbon atoms in ring ...	3	4	7	17
Angular distortion (Baeyer) ...	+24° 44′	+9° 44′	−9° 33′	−24° 41′

But the corresponding 3- and 4-membered ring compounds would not, of course, survive such treatment.

Formation of Large Carbon Rings.—If, however, we consider, not stability, but tendency to formation, the difference between the small and the large rings is in the opposite sense. In contrast to the numerous methods by which 3- and 4-membered carbon rings may be prepared, the rings containing from 10 to 18 carbon atoms are accessible by only one method, and in small yield. The yields obtained by the distillation of thorium and calcium salts appear to show a maximum at *cyclo*hexanone :

Acid.	Th-salt (%).	Ca-salt (%).	C-atoms in ring.
Glutaric	0	0	4
Adipic	15	45	5
Pimelic	70	40–50	6
Suberic	50	35	7
Azelaic	20	5	8
Sebacic	1·5	<1	9

Data such as these may be partly correlated by assuming [16] that the formation of a ring depends on the product of two factors. One, connected with the distance between the two ends of a chain, will favour the production of small rings; the extreme case of the

[13] *Ann. Report*, 1924, **21**, 92. Compare J. W. Baker, *J.*, 1925, **127**, 1678; W. A. Wightman, *ibid.*, p. 1421; *J.*, 1926, 2541; F. W. Kay and N. Stuart, *ibid.*, p. 3038; W. Hückel, *Annalen*, 1926, **451**, 109; W. Hückel and H. Friedrich, *ibid.*, p. 132.

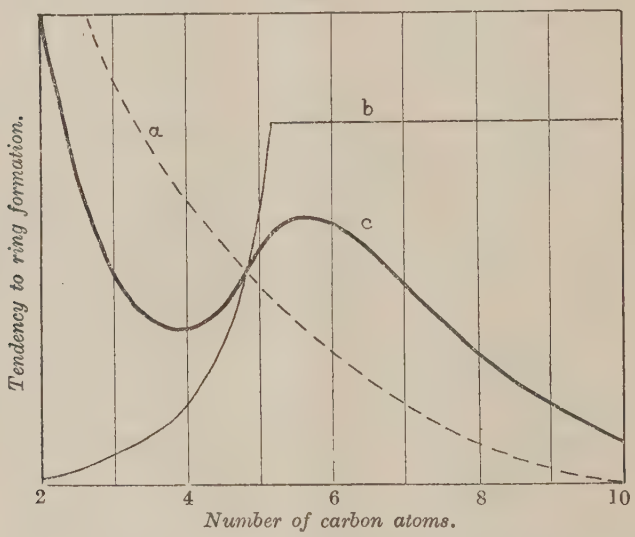
[14] L. Ruzicka, W. Brugger, M. Pfeiffer, H. Schinz, and M. Stoll, *Helv. Chim. Acta*, 1926, **9**, 499; **A.**, 727.

[15] *Idem, ibid.*

[16] *Idem, ibid.*

operation of this factor would be represented by the formation of a double bond. The second factor will depend on the intrinsic stability of the ring, and will favour the production of strainless rings. The idea may be expressed graphically (Fig. 1): curve *a* represents the "distance factor," and it falls continuously with increasing length of the chain which is to be closed; curve *b* depicts the "strain factor," rising to a point between C_5 and C_6 and thereafter remaining constant, since the higher rings are strainless. Apart from these main features, the curves are, of course, arbitrary, and the resultant curve, *c*, represents some kind of mean between them, with its minimum at C_4 and its maximum between C_5 and C_6, corresponding with the observed data.

FIG. 1.



Physical Properties of Large Rings.—The increment in molecular volume at 20° of the normal aliphatic hydrocarbons, for each added CH_2-group, is 16 units and is constant from C_4 to C_{18}; the increment for the alicyclic hydrocarbons is not constant, but rises from about 13 to 16 over the same range. Again, the increment for the open-chain ketones is approximately $16\frac{1}{2}$ units and is sensibly constant; that for the cyclic ketones, on the other hand, rises between C_4 and C_{18} from 14 to $16\frac{1}{2}$. The following table illustrates these contrasts: [17]

[17] L. Ruzicka, W. Brugger, M. Pfeiffer, H. Schinz, and M. Stoll, *Helv. Chim. Acta*, 1926, **9**, 499; **A.**, 727.

No. of C-atoms.	Hydrocarbons $\Delta(M/d)$. Aliphatic.	Cyclic.	Ketones $\Delta(M/d)$. Aliphatic.	Cyclic.
4				
5	15·0	12·5	16·0	13·7
6	16·0	14·0	17·3	14·8
7	16·5	13·0	16·8	14·5
8	15·4	13·2	16·8	13·6
9	16·1		15·7	14·9
10	16·2		17·2	Mean 15·6
11	16·0	Mean 15·3	16·5	
12	15·9		Mean 16·0	
13	16·7			Mean 15·6
14	15·7		Mean 16·7	
15	16·9			
16	15·9	Mean 16·5	15·3	16·6
17	16·5	—	17·2	16·6
18	16·2		Mean 16·2	16·7
19	—	—		—

That the increments for the cyclic series should, in each case, from about C_{10} upwards, be within a unit of the figure characteristic of the corresponding aliphatic homologues, agrees, of course, with the hypothesis of multiplanar configurations; for these large rings will be wholly collapsed, and so crumpled that the volume required by an added CH_2-group will be the same as if it were added to a similarly crumpled aliphatic chain. In the intermediate rings from C_6 to C_{10}, the collapse is probably only partial, in the sense that a certain amount of space inside the ring, and dependent on the existence of the ring, becomes a more or less permanent addition to the volume occupied by the molecule. In the rings below C_6 distortion during thermal agitation is largely eliminated; the molecule now has a characteristic shape and the internal space now represents a quite definite addition to the volume occupied, part of which is assigned to each of the constituent methylene groups. Thus as we *descend* the series the volume of the molecule increases relatively (*i.e.*, decreases more slowly than it otherwise would) and the decrements become smaller.

The matter may be illustrated in another way. The volume contribution of CH_2 in a hydrocarbon (open-chain) is known to be 16·1 units. The molecular volumes of the *cyclo*paraffins, divided in each case by the number of CH_2 groups in the ring, are as follows:

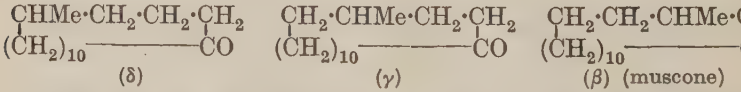
No. of CH_2 groups (n) . . .	4	5	6	7	8	. . .	15	17
$(M/d)/n$	20·4	18·8	18·0	17·3	16·8	. . .	16·1	16·1

The numbers for the smaller rings (4—8) obviously represent the volume *occupied* by the CH_2 group, *plus* a share of the internal

space; in the 15- and 17-membered rings there is no internal space and the normal value obtains.

Occurrence of Large Rings in Nature: Muscone and Civetone.—Until this year no monocyclic [18] compound containing a ring of more than six carbon atoms had been proved to occur in the animal or the vegetable kingdom.[19] It is now clear, however, that muscone from the musk-deer contains a ring of fifteen carbon atoms,[20] whilst civetone from the civet cat contains a 17-membered carbon ring.[21]

Muscone, a liquid ketone, $C_{16}H_{30}O$ (semicarbazone, m. p. 134°), was isolated from musk by H. Walbaum.[22] It is saturated and hence monocyclic, and its optical activity shows that it must contain an asymmetric carbon atom. Since racemisation does not occur on conversion into the sodio-derivative of the enol, the centre of asymmetry cannot be a tertiary carbon adjacent to the ketone group. Oxidation yields decane-$\alpha\kappa$-dicarboxylic acid, from which it follows that an uninterrupted chain of at least 10 methylene groups must be present. Several 13-, 14- and 15-ring formulæ are consistent with these conclusions, but the identity of the odour with that of certain methyl*cyclo*pentadecanones, which were prepared by distillation of the appropriate thorium salts, was taken as indicating a 15-ring structure, and the surmise was confirmed by reducing muscone to methyl*cyclo*pentadecane, $CH_3{\cdot}CH{<}(CH_2)_{14}$, which was also prepared from one of the synthetic ring ketones. It remained to determine the relative positions of the methyl and ketone groups, the possibilities being represented by β- γ-, and δ-methyl*cyclo*pentadecanone:



Final identification was rendered difficult by the fact that muscone and many of its more closely related derivatives are optically active. The γ-methyl formula was excluded as improbable, because the m. p. of the semicarbazone of a synthetic (inactive) specimen of this ketone was lowered by admixture with muscone semicarbazone; and a decision in favour of the β-methyl formula was made on the ground that the methyltridecane-$\alpha\omega$-dicarboxylic acids, obtained by

[18] The qualification is intended to exclude bicyclic heterocyclic compounds with a *single homocyclic* ring, like tropine and ψ-pelletierine, and also bridged homocyclic compounds such as the carenes.

[19] But *cyclo*heptane occurs in Caucasian petroleum.

[20] L. Ruzicka, *Helv. Chim. Acta*, 1926, **9**, 715; **A.**, 1142.

[21] *Idem, ibid.*, p. 230; **A.**, 614.

[22] *J. pr. Chem.*, 1906, **73**, 488; *A.*, 1906, **i**, 595.

oxidation of muscone and its benzylidene derivative, although optically active, agreed much more closely in their properties with the synthetic α- and β-methyl acids, $CO_2H{\cdot}CHMe{\cdot}(CH_2)_{12}{\cdot}CO_2H$ and $CO_2H{\cdot}CH_2{\cdot}CHMe{\cdot}(CH_2)_{11}{\cdot}CO_2H$, to be expected from a ketone having the β-methyl formula, than with the isomeric γ- and δ-methyl acids, $CO_2H{\cdot}(CH_2)_2{\cdot}CHMe{\cdot}(CH_2)_{10}{\cdot}CO_2H$ and

$$CO_2H{\cdot}(CH_2)_3{\cdot}CHMe{\cdot}(CH_2)_9{\cdot}CO_2H,$$

corresponding with the δ-methyl ketone structure.[23] This proof of the constitution is admittedly not quite complete.

Civetone, an unsaturated ketone (m. p. 31°) having the composition $C_{17}H_{30}O$, was obtained from civet by Sack.[24] It contains one double linking and, therefore, a single ring, and the character of the ring is revealed by the fact that the dihydro-derivative, obtained by catalytic reduction, is identical with synthetic *cyclo*heptadecanone (m. p. 63°). The position of the double linking follows from the observation that azelaic acid, but no higher polymethylene-αω-dicarboxylic acid, is formed on oxidation.

This determines the formula, and it is interesting from the biological point of view to compare it with that of oleic acid and to speculate on the possibility of their biochemical interconversion.[21]

$$\begin{matrix} CH{\cdot}(CH_2)_7{\cdot}CH_3 \\ \| \\ CH{\cdot}(CH_2)_7{\cdot}CO_2H \\ \text{(oleic acid)} \end{matrix} \longrightarrow \begin{matrix} CH{\cdot}(CH_2)_7 \\ \| \quad >CO \\ CH{\cdot}(CH_2)_7 \\ \text{(civetone)} \end{matrix}$$

Stereochemistry. The Diphenyl Problem.

A remarkable outcome of work published during the year is the proof that a coincidence of errors was directly responsible for Christie and Kenner's fundamental discovery (1922) that certain derivatives of diphenic acid are capable of optical resolution. For the past 4 years, however, the same errors have obscured the whole appearance of the stereochemical problem thus opened. Now, with their rectification, effected in a series of papers published in rapid succession, the whole problem enters upon a new phase.

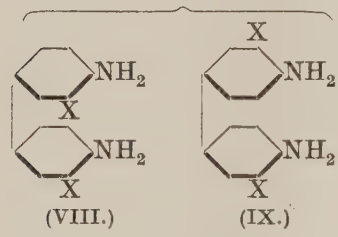
$$\begin{matrix} C_6H_4{\cdot}NH \\ | \quad >CO \\ C_6H_4{\cdot}NH \end{matrix} \quad \text{(I.)} \qquad \begin{matrix} C_6H_4{\cdot}NH \\ | \quad >CS \\ C_6H_4{\cdot}NH \end{matrix} \quad \text{(II.)} \qquad \begin{matrix} C_6H_4{\cdot}NH{\cdot}CO \\ | \\ C_6H_4{\cdot}NH{\cdot}CO \end{matrix} \quad \text{(III.)} \qquad \begin{matrix} C_6H_4{\cdot}NH{\cdot}CO \\ | \quad >C_6H_4 \\ C_6H_4{\cdot}NH{\cdot}CO \end{matrix} \quad \text{(IV.)}$$

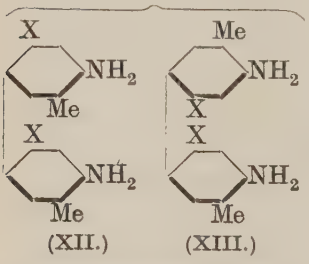
$$\begin{matrix} C_6H_4{\cdot}NEt{\cdot}CO \\ | \quad >C_6H_4 \\ C_6H_4{\cdot}NEt{\cdot}CO \end{matrix} \quad \text{(V.)} \qquad \begin{matrix} C_6H_4{\cdot}NH \\ | \quad >CH{\cdot}C_6H_4{\cdot}NO_2 \\ C_6H_4{\cdot}NH \end{matrix} \quad \text{(VI.)}$$

(VII.)

[23] L. Ruzicka, *Helv. Chim. Acta*, 1926, **9**, 1008.
[24] E. Sack, *Chem. Ztg.*, 1915, **39**, 538; *A.*, 1915, i, 888.

The reported existence of the ring compounds of benzidine, (I)—(VI), which had been described by a number of independent workers,[25] led F. Kaufler,[26] in 1907, to propose his folded structure (VII) for the diphenyl system. J. C. Cain and his co-workers (1912—14), believing that they had established the existence of two *o*-dinitrobenzidines and two pairs of *m*-dinitrotolidines [27] (VIII—XIII), adopted the Kaufler formula as an explanation of these conventionally inexplicable isomerides, and supported their conclusions by the preparation of further "Kaufler compounds" (types XIV and XV) from benzidine and tolidine by condensation with the α-diketones glyoxal and benzil.[28]





$C_6H_4{\cdot}N{:}CR$ / $C_6H_4{\cdot}N{:}CR$ (XIV.)

$C_6H_3Me{\cdot}N{:}CR$ / $C_6H_3Me{\cdot}N{:}CR$ (XV.)

[X = NO_2]

Independently of these investigations, J. Schmidt and A. Kämpf had recorded experiments [29] which appeared definitely to orient an already known dinitrodiphenic acid (prepared from a dinitration product of phenanthraquinone [30]) as the 6 : 6′-derivative (XVI). When, therefore, J. Kenner and W. V. Stubbings [31] obtained a different

[25] W. Michler and A. Zimmermann, *Ber.*, 1881, **14**, 2178; *A.*, 1882, i, 182; J. Borodin, *Jahresb.*, 1860, 356; *Z. Chem. Pharm.*, 1860, 641; J. Strakosch, *Ber.*, 1872, **5**, 240; G. Koller, *Ber.*, 1904, **37**, 2882; *A.*, 1904, i, 778; H. Schiff and A. Vanni, *Annalen*, 1890, **258**, 363; *A.*, 1890, 1297; J. Barzilowski, *J. Russ. Phys. Chem. Soc.*, 1891, **23**, 69; *A.*, 1892, 854.

[26] *Annalen*, 1907, **351**, 151; *A.*, 1907, i, 307; *Ber.*, 1907, **40**, 3250; *A.*, 1907, i, 794.

[27] *J.*, 1912, **99**, 2298; 1914, **103**, 1442.

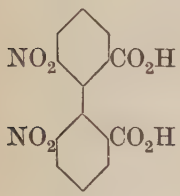
[28] *Ibid.*, 1914, p. 1437.

[29] *Ber.*, 1903, **36**, 3745; *A.*, 1904, i, 71.

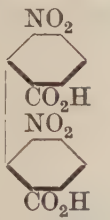
[30] G. Schulze, *Annalen*, 1880, **203**, 95; *A.*, 1880, 814.

[31] *J.*, 1921, **119**, 593.

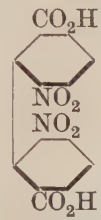
6 : 6′-dinitrodiphenic acid (from 2-iodo-3-nitrobenzoic acid and copper powder) they naturally concluded that they were possibly dealing with a pair of "Kaufler stereoisomerides" (XVII and XVIII). The allocation of configurations presented no difficulty, for the new compound on reduction gave the dilactam (XIX), whilst the old one had already been formed from a phenanthraquinone and converted (by Schmidt and Kämpf) into carbazole.[32] It followed that the new acid might be capable of optical resolution :



(XVI.)



(XVII, *cis*, non-resolvable.)

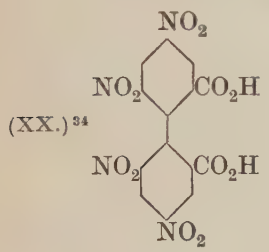


(XVIII, *trans*, resolvable.)

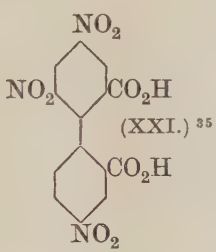
(XIX.)

and it was.[33]

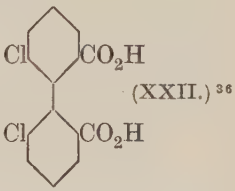
Since then, the following compounds (XX—XXIV) have been resolved, though none has been obtained in more than one inactive (racemic) modification :



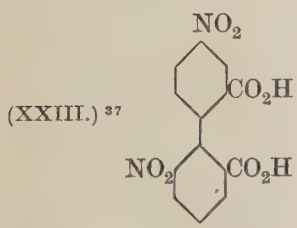
(XX.)[34]



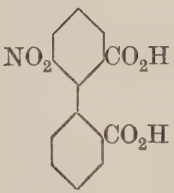
(XXI.)[35]



(XXII.)[36]



(XXIII.)[37]



(XXIV.)[38]

[32] *Loc. cit.*

[33] G. H. Christie and J. Kenner, *J.*, 1922, **121**, 614.

[34] *Idem*, *ibid.*

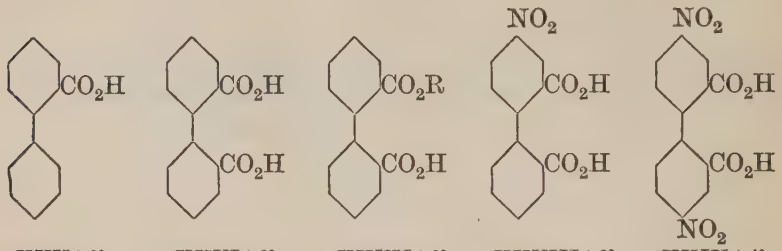
[35] *Idem*, *J.*, 1923, **123**, 779.

[36] G. H. Christie, C. W. James, and J. Kenner, *ibid.*, p. 1948.

[37] G. H. Christie, A. Holderness, and J. Kenner, *J.*, 1926, 671; **A.**, 518.

[38] F. Bell and J. Kenyon, *Chem. and Ind.*, 1926, **45**, 864; compare G. H. Christie, *ibid.*, p. 934.

In addition, the following have been investigated with the object of resolving them, but have so far resisted resolution (XXV—XXIX):



(XXV.)[39] (XXVI.)[39] (XXVII.)[39] (XXVIII.)[39] (XXIX.)[40]

In 1920, C. V. Ferriss and E. E. Turner[41] investigated Cain's supposed ring compounds (types XIV and XV), and were unable to confirm the conclusions which had been drawn with regard to them. This year, Turner and his collaborators have systematically overhauled the whole of the evidence on which Kaufler based his space formula, with the result that no part of it survives.[42] The carbonyl compound (I) contains a free amino-group and is probably (IA); the thiocarbonyl compound (II) is certainly (IIA); the oxalyl compound (III) contains a free amino-group; the phthalyl compound (IV) is really (IVA); the phthalyldiethyl derivative is not a chemical individual; the nitrobenzylidene compound (VI) has the structure (VIA).[43] In addition, Cain's condensation product from benzidine and benzil is really (XIVA),[44] whilst the glyoxal condensation products, which also were formulated as ring compounds, are hard, brown resins of unknown molecular weight.

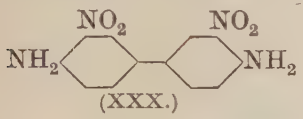
$[NH_2\cdot(C_6H_4)_2\cdot NH]_2CO$ (IA.) $NH_2\cdot(C_6H_4)_2\cdot N{:}C{:}S$ (IIA.) $NH_2\cdot(C_6H_4)_2\cdot N{<}\begin{matrix}CO\\CO\end{matrix}{>}C_6H_4$ (IVA.)

$NH_2\cdot(C_6H_4)_2\cdot N{:}CH\cdot C_6H_4\cdot NO_2$ (VIA.) $COPh\cdot CPh{:}N\cdot(C_6H_4)_2\cdot N{:}CPh\cdot COPh$ (XIVA.)

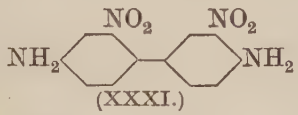
Next, it is proved[45] that the most fully investigated of Cain's pairs of isomerides, namely, the two dinitrobenzidines (VIII and IX), are, in fact, structurally distinct (XXX and XXXI). The observation that they give different tetra-amines on reduction[46]

[39] F. Bell and J. Kenyon, *loc. cit.*; *J.*, 1926, 2705; **A.**, 1241; *ibid.*, p. 3044.
[40] G. H. Christie, *loc. cit.* [41] *J.*, 1920, **117**, 1140.
[42] R. J. W. Le Fèvre and E. E. Turner, *J.*, 1926, 2476; **A.**, 1131.
[43] H. G. Dennett and E. E. Turner, *ibid.*, p. 478; **A.**, 391.
[44] R. J. W. Le Fèvre and E. E. Turner, *loc. cit.*
[45] *Idem, ibid.*, p. 1759; **A.**, 946.
[46] O. L. Brady and G. P. McHugh, *J.*, 1923, **123**, 2047.

is therefore explicable, but the statement that these yield identical diquinoxalines is, by implication, an error. Independently, it is also shown [47] that Schmidt and Kämpf's proof of the constitution of the long-known dinitrodiphenic acid is without foundation, the pair of compounds (XVII and XVIII) handled by Kenner and Stubbings being actually position isomerides (XXXII and XXXIII); and that the individual (XXXIII) previously regarded as probably belonging to the *cis*-, non-resolvable class, can, in fact, be resolved. The two pairs of supposedly stereoisomeric dinitrotolidines (X—XIII) still remain unchallenged (except by implication), but the indirect evidence is very strong that the recorded observations on these compounds are to be accounted for in some other way than that chosen by their discoverers.

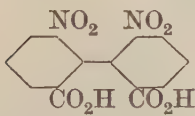


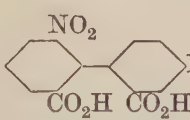
(XXX.)



(XXXI.)

(XXXII.)





(XXXIII.)

Thus, not only the phenomenon which Kaufler's space-formula was invented to explain, but also that which it was afterwards resuscitated to interpret, do not exist; and the formula itself has lost caste.[48] The sole remaining relevant fact is that six substituted diphenic acids have been resolved, and it is thus possible to view the matter afresh.

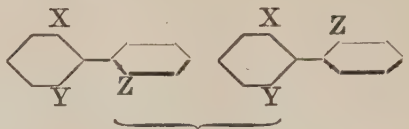
Attempts are being made to do so. E. E. Turner and R. J. W. Le Fèvre [49] attribute the possibility of optical resolution to a repulsion between ortho-substituents which tends to push the planes of the rings apart (by rotation about the internuclear bond), whilst the attraction between the ortho-carbon atoms tends to limit the angular separation; the "repulsion" is regarded as either electrical or spatial in origin:

(enantiomorphous forms)

F. Bell and J. Kenyon suggest [50] that, owing either to their electrical character or to their size, *two* ortho-groups, (X) and (Y),

[47] G. H. Christie, A. Holderness, and J. Kenner, *loc. cit.*
[48] Compare R. Kuhn and F. Zumstein, *Ber.*, 1926, **59**, 488; **A.**, 513.
[49] *Chem. and Ind.*, 1926, **45**, 831. [50] *Ibid.*, p. 864; *J.*, 1926, 3045.

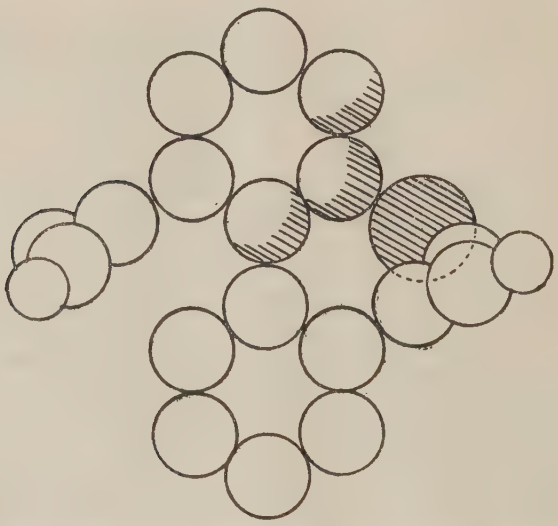
act as obstacles to the passage of an ortho-group (Z) on the other nucleus, thus preventing interconversion of the optical antipodes :



(enantiomorphous forms)

W. H. Mills [51] holds a similar view, and in addition points out that, if it is legitimate to assume a considerable degree of molecular rigidity, spatial considerations alone are able to provide an

FIG. 2.*



* Reproduced by permission from *Chemistry and Industry*.

explanation for all the optically active diphenyl derivatives hitherto recorded. Thus in 6-chlorodiphenic acid (Fig. 2) the carboxyl group attached to the lower nucleus can pass neither the chlorine atom (large circle) nor the other carboxyl group, and hence is confined to a limited region in front of the plane of the upper ring; in the enantiomorph, similarly depicted, the corresponding carboxyl group would be always behind the plane of the upper ring : [52]

Actually, 6-chlorodiphenic acid has not yet been investigated, but

[51] *Chem. and Ind.*, 1926, **45**, 883, 905.

[52] The nuclear hydrogen atoms are omitted from the figure, as it is assumed that they would be too small to limit the mutual relative rotations of the phenyl rings by the mechanism discussed.

the argument applies to all the diphenic acids which have hitherto been obtained in optically active modifications (XVI and XX—XXIV). It should be stated that molecular dissymmetry originating in co-axial but non-coplanar nuclei was one of the possibilities originally envisaged by Christie and Kenner; but the "obstacle theory" of the mechanism whereby the enantiomorphous forms maintain their individuality appears to be a definite advance, because, not only does it afford a satisfying explanation of all the recorded positive observations, but it also shows why the attempted resolutions of other diphenyl derivatives (XXV—XXIX) were unsuccessful: for in each of these at least one of the three ortho-groups which, according to the hypothesis, are required to produce stable enantiomorphs is absent from the molecule.

On the assumption that the ortho-substituents are such as will form effective obstacles to the relative rotation of the phenyl nuclei, resolvable diphenyl derivatives should conform to the types

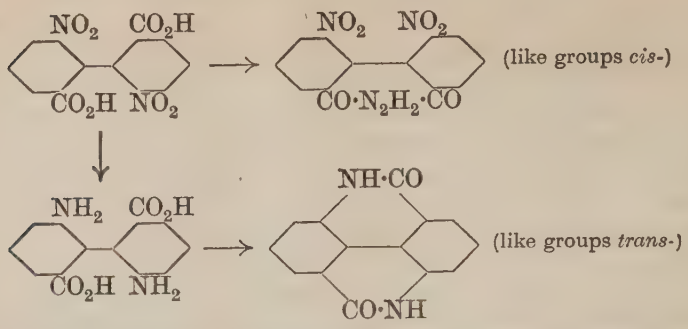
where A and B are different from each other, and X and Y also are different from each other, although neither is otherwise precluded from identity with A or B. The case is, in fact, comparable with that of allene derivatives,

$$\begin{matrix} A \\ B \end{matrix}\!\!>\!C\!=\!C\!=\!C\!<\!\!\begin{matrix} X \\ Y \end{matrix},$$

the essential condition being the indirect attachment to the centre of dissymmetry of two pairs of unlike groups by an arrangement which prevents their occupying a common plane; but, in diphenyl derivatives, the centre of dissymmetry resides, not in an atom, but in a bond. It remains to be seen whether small, but highly polar, groups (*e.g.*, fluorine or ionised hydroxyl in 6 : 6′-difluorodiphenic acid or an alkaline solution of 6 : 6′-dihydroxydiphenic acid), which from the purely spatial point of view would hardly be expected to constitute effective obstacles, are also capable of imparting potential optical activity to the molecule.

It may be added that certain reactions which caused Kenner and Stubbings [53] to postulate *cis-trans* inversion—for example, the formation of a hydrazide from the same dinitrodiphenic acid which when reduced yields the dilactam:

[53] *Loc. cit.* Compare also E. E. Turner and R. J. W. Le Fèvre, *loc. cit.*



are readily explained on the new theory; because an ortho-group attached to one phenyl nucleus will, in its mean position, be approximately equidistant from the two ortho-positions of the other nucleus, and the formation of a ring in either direction should be possible.

Other Stereochemical Problems.—Definite advances have been made during the year in other stereochemical problems, but for the most part along lines already laid down by past work.

The optical resolution of sulphinic esters, reported last year,[54] has been followed up by the resolution of the two sulphoxides (XXXIV) and (XXXV) [55] and the sulphilimine (XXXVI).[56]

$$(p)NH_2\cdot C_6H_4\cdot \overset{+}{S}\overset{-}{O}\cdot C_6H_4\cdot CH_3(p) \qquad (m)CO_2H\cdot C_6H_4\cdot \overset{+}{S}\overset{-}{O}\cdot CH_3$$
(XXXIV.) (XXXV.)

(XXXVI.) $CO_2H\cdot C_6H_4\diagup \begin{matrix} \\ CH_3 \end{matrix} \!\!> \overset{+}{S}\overset{-}{\cdot}N\cdot SO_2\cdot C_7H_7$

Every case of this kind naturally strengthens the evidence of the stability of the sulphonium octet; but the question why the latent fourth valency of sulphonium sulphur should so rigidly maintain its place in the tetrahedral arrangement, whilst the corresponding latent valency in neutral tervalent nitrogen does not appear to do so, remains for the present unanswered (except for the suggestion that it has something to do with the positive charge).

Brady and Bishop's experiment, reported last year,[57] on *iso*oxazole ring closure with aromatic aldoximes, has now been paralleled for ketoximes by Meisenheimer and his collaborators with corresponding results,[58] which therefore favour the general proposal to

[54] *Ann. Report*, 1925, **22**, 111.

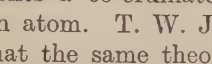
[55] P. W. B. Harrison, J. Kenyon, and H. Phillips, *J.*, 1926, 2079; **A.**, 1030.

[56] S. G. Clarke, J. Kenyon, and H. Phillips, *J.*, 1927, 188.

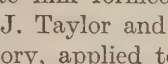
[57] *Ann. Report*, 1925, **22**, 107.

[58] J. Meisenheimer, P. Zimmermann, and M. von Kummer, *Annalen*, 1926, **446**, 205; **A.**, 405.

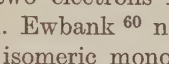
invert oxime configurations. A special feature of the year's work on this subject is, however, the fact that it has been attacked from the physical side. N. V. Sidgwick has shown [59] that the solubility and volatility of the enolic forms of β-diketones and β-ketonic esters can be accounted for by the structure (XXXVII), where the arrow represents a co-ordinate link formed by two electrons from the oxygen atom. T. W. J. Taylor and E. K. Ewbank [60] now point out that the same theory, applied to the isomeric monoximes of α-diketones, satisfactorily explains, not only their physical properties, but also their chemical differences; for the isomeride which is the more volatile and soluble in non-polar solvents is that which shows least carbonyl reactivity. This view, of course, implies definite stereochemical configurations for each pair of oxime, and in the case of benzil the configurations so arrived at (XXXVIII and XXXIX) are identical with those deduced by Meisenheimer from the oxidative fission of triphenyl*iso*oxazole : [61]



(XXXVII.)



(XXXVIII; α-.)

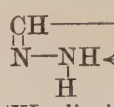


(XXXIX; β-.)

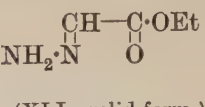
The fact that only α-benzilmonoxime gives metallic co-ordination compounds with iron, cobalt, and copper is accounted for by the hypothesis that an attack by the metal cation on the carbonyl oxygen atom constitutes the first step in the formation of these compounds. On the whole, the balance of evidence seems at present to be more heavily loaded on the side of the inversion of the customary oxime configurations, but O. L. Brady and R. F. Goldstein [62] record observations showing that aromatic α-aldoximes (*i.e.*, the isomerides which *less* readily yield nitriles) are stronger acids than the isomeric β-aldoximes, and that is a weight in the other pan.

Taylor and Ewbank apply their considerations to the allied problem of the configuration of hydrazones, with very satisfactory results. Thus of the two hydrazones of glyoxylic ester,[63] one is a liquid and is more volatile and less soluble in water than the other, and the liquid isomeride has the normal molecular weight in benzene, whilst the other is a solid and is associated in solution. The configurations (XL) and (XLI) follow, and accord well with the fact that, whereas the liquid form reacts only slowly with phenylcarbimide and not at all with diphenylketen, the solid isomeride combines readily with both these reagents :

[59] *J.*, 1925, **127**, 907. [60] *Ibid.*, 1926, 2818.
[61] *Ann. Report*, 1925, **22**, 106. [62] *J.*, 1926, 1918; **A.**, 1039.
[63] H. Staudinger, L. Hammett, and J. Siegwart, *Helv. Chim. Acta*, 1921, **4**, 228; *A.*, 1921, i, 326.



(XL; liquid form.)



(XLI; solid form.)

Other examples discussed are the camphorquinone hydrazones investigated by M. O. Forster and A. Zimmerli,[64] and in this connexion it should be mentioned that the following statement, which occurs in last year's Report,[65] is misleading: "Pairs of stereoisomeric hydrazones have frequently been described, but no method of orientation in which any degree of confidence could be placed had until recently been evolved." The Reporter had overlooked the fact that in the course of the work referred to above (1910—1911) Forster and Zimmerli had oriented pairs of hydrazones and substituted hydrazones by the method of ring formation which has been applied only within comparatively recent years to other pairs of hydrazones and to the oximes.

Further work on the truxillic acids has led to the revision of a formula previously proposed for ε-truxillic acid,[66] and this, together with a new investigation of γ-truxillic acid,[67] confirms the allocation of configurations amongst the five truxillic acids given in the Annual Report for 1924 (p. 95).

Optical Activity Dependent on Co-ordinated Beryllium, Copper, and Zinc.—An important paper on this subject has just appeared. T. M. Lowry and H. Burgess [68] had observed that beryllium benzoylcamphor, when dissolved in chloroform or benzene, shows mutarotation, which they ascribed to the gradual disappearance of optical activity associated with the beryllium atom; they pointed out that this atom would probably act as a centre of dissymmetry in a spiran arrangement such as that represented in Fig. 3.

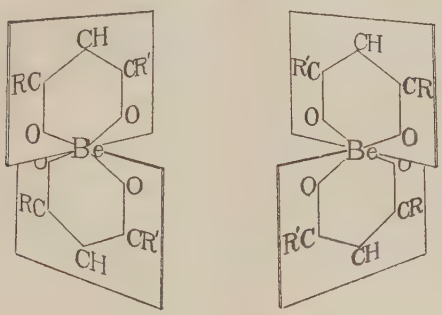
W. H. Mills and R. A. Gotts [69] have now shown that an inactive β-diketone, namely benzoylpyruvic acid, $C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CO_2H$, which in itself is devoid of molecular dissymmetry, can acquire it on conversion into its beryllium derivative. Two brucine salts of this derivative were prepared, and these, when dissolved in chloroform, exhibited changes of rotatory power which were substantially equal and opposite; also the difficult task of removing the alkaloid without destroying the sensitive optical activity associated with the beryllium atom was accomplished with a large degree of success.

[64] *J.*, 1910, **97**, 2156. Compare *J.*, 1911, **99**, 478.
[65] *Ann. Report*, 1925, **22**, 111.
[66] R. Stoermer, J. Neumaerker, and R. Schmidt, *Ber.*, 1925, **58**, 2707; **A.**, 1926, 290.
[67] R. Stoermer and F. Fretwurst, *ibid.*, p. 2718; **A.**, 1926, 291.
[68] *J.*, 1924, **125**, 2081.
[69] *Ibid.*, 1926, 3121.

The tetrahedral arrangement thus established for the four oxygen atoms surrounding the beryllium atom (Fig. 3) corresponds with that deduced for the crystalline state by Sir W. H. Bragg and G. T. Morgan [70] from their study of basic beryllium acetate :

Alkaloidal salts of the analogous copper and zinc derivatives of benzoylpyruvic acid were also prepared, and they showed an optical behaviour closely similar to that of the beryllium compound; there can be no doubt that this is due to a corresponding cause. Since copper and zinc are both capable of forming 6-co-ordinated derivatives in which the groups are almost certainly octahedrally disposed, these observations are of considerable interest because they indicate that when two of the six co-valencies become latent the remaining four assume a tetrahedral configuration. It is pointed out that a

FIG. 3.



similar conclusion must apply to arsenic in view of the optical resolution of tripyrocatechylarsenic acid, $H[As(C_6H_4O_2{:})_3]$,[71] and of *p*-carboxyphenylmethylethylarsine sulphide, $R_1R_2R_3AsS$.[72]

Orienting Effects in Benzene Substitutions.

A considerable amount of attention has recently been devoted to the study of the mechanism of aromatic substitution. Definite experimental and theoretical advances have been made, but at the same time it has become increasingly evident that a completely satisfactory interpretation is still indefinitely remote. In the meantime, the complexity of the subject seems to render an interim report desirable.

(i) *Orienting Effect of Poles.*—(The seat of the charge in a complex ion may conveniently be termed a " pole.")

The established phenomenon of intramolecular ionisation (*e.g.*, in semipolar double linkings) and the probable occurrence of both

[70] *Proc. Roy. Soc.*, 1923, [*A*], **104**, 437; *A.*, 1924, i, 7.
[71] A. Rosenheim and W. Plato, *Ber.*, 1925, **58**, 2000; *A.*, 1925, i, 1412.
[72] *Ann. Report*, 1925, **22**, 113.

incipient intramolecular ionisation and incipient ionic dissociation in organic molecules render impossible a sharp distinction between electrically charged and uncharged atoms. Nevertheless, those atoms which carry one or more of the *integral* charges created by the ionic dissociation of a strong electrolyte may be conveniently considered together in regard to their orienting effects, because these probably represent the extreme (and therefore most easily apprehended) examples of phenomena which other atoms are also able to bring about in various lesser degrees according to their several electrochemical characters.

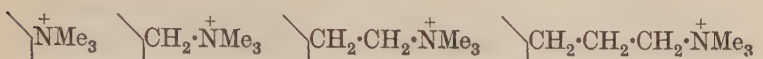
Positive poles. The orienting influence of a positive pole directly attached to the nucleus is readily stated : it is exclusively *m*-directing so far as is known. The main established examples are the bromination of phenyltrimethylammonium bromide,[73] and the nitration of phenyltrimethylammonium nitrate,[74] of diphenyliodinium nitrate,[75] triphenylhydroxyphosphonium nitrate,[76] triphenylantimony dinitrate,[77] triphenylbismuth dinitrate,[78] and diphenyl-lead dinitrate.[79] In these instances, the observed orienting effects are substantially identical, despite the fact that the charged atom ranges in atomic weight and electrochemical character from nitrogen to lead and from lead to iodine. Further, since in no case has any *o*- or *p*-isomeride been isolated, it appears that the side-chains present in all these compounds are amongst the strongest *m*-directing groups known. The inference, that a positive pole attached to the nucleus is *m*-orienting independently of the nature of the charged atom, has been drawn by D. Vorländer.[80]

The introduction of successive saturated carbon atoms (*e.g.*, $-CH_2-$ groups) between a positive pole and the nucleus diminishes the *m*-orienting effect. Ionised benzylammonium salts are nitrated largely, but not wholly, in the *m*-position;[81, 82, 83] β-phenylethylammonium salts, on nitration, also undergo *m*-substitution, but to a smaller extent; and with γ-phenylpropylammonium salts the proportion of *m*-derivative is smaller still.[84] The steady diminution

[73] D. Vorländer and E. Siebert, *Ber.*, 1919, **52**, 283; *A.*, 1919, i, 319.
[74] *Idem, ibid.*
[75] D. Vorländer and K. Büchner, *Ber.*, 1925, **58**, 1898; *A.*, 1925, i, 1255.
[76] A. Michaelis and H. v. Soden, *Annalen*, 1885, **229**, 324; *A.*, 1885, 1134; F. Challenger and J. F. Wilkinson, *J.*, 1924, **125**, 2675; *A.*, 1925, i, 172.
[77] G. T. Morgan and F. M. G. Micklethwait, *J.*, 1911, **99**, 2286.
[78] D. Vorländer and E. Schroedter, *Ber.*, 1925, **58**, 1900; *A.*, 1925, i, 1255.
[79] D. Vorländer and E. Spreckels, *ibid.*
[80] D. Vorländer, *ibid.*, 1919, **52**, 262; *A.*, 1919, i, 319.
[81] B. Flürscheim and E. L. Holmes, *J.*, 1926, 1562; **A.**, 830.
[82] H. R. Ing and R. Robinson, *ibid.*, p. 1655; **A.**, 946.
[83] F. R. Goss, C. K. Ingold, and I. S. Wilson, *ibid.*, p. 2440; **A.**, 1132.
[84] F. R. Goss, W. Hanhart, and C. K. Ingold, *J.*, 1927, 250.

in the amount of *m*-substitution with increasing length of the carbon chain may be illustrated by the following series :

Nitration of :

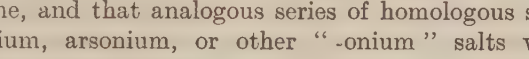


Approximate proportion of m-*nitro-derivative :*

(100%.) (88%.) (19%.) (5%.)

These are the only examples which are at present available to illustrate the principle, but there can be little doubt that it is a general one, and that analogous series of homologous sulphonium, phosphonium, arsonium, or other " -onium " salts would show corresponding relationships.

There is reason to assume that the introduction of unsaturated carbon atoms (*e.g.*, $-CH=CH-$ groups) between a positive pole and the benzene nucleus would cause an even more rapid damping out of the *m*-orienting influence. As a matter of fact, salts of the types

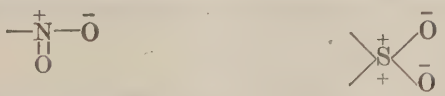


do not appear to have been investigated, but the close correspondence between ammonium salts and nitro-compounds (below) suggests that even in the first member of such a series the *m*-orienting effect of the positive pole would be reduced to a very small order.

Negative poles. The powerful *op*-directing influence of a negative pole has long been familiarly illustrated by the rapid and exclusive *op*-substitution of phenols and thiophenols in alkaline solution.

No very simple examples are available to illustrate the probable decrease in the intensity of the effect with increasing distance between the negative pole and the nucleus, but a decrease of *op*-reactivity can be inferred from general experience, for instance, the circumstance that benzyl mercaptan has never been observed to couple with diazo-salts or undergo *op*-halogenation in alkaline solution.

Dipoles. The semipolar double linkings in the nitro- and sulphone groups furnish clear cases of established intramolecular ionisation : [85]

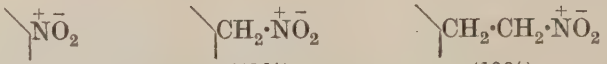


The orienting effect of such groups, in so far as it arises from the ionic charges present, might be expected to be that of a free pole

[85] S. Sugden, J. B. Reed, and H. Wilkins, *J.*, 1925, **127**, 1525; *A.*, 1925, ii, 936.

corresponding with the end of the dipole nearer the nucleus, somewhat diminished, however, by the partly compensating contrary influence of the more distant pole of opposite sign.

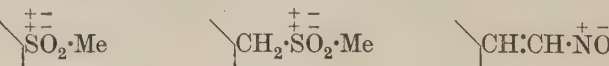
In illustration of this principle, the estimated proportions in which *m*-substitution occurs in the nitration of nitrobenzene,[86] phenylnitromethane, and β-phenylnitroethane may be compared with the corresponding data for the ammonium salts referred to above :[87]



(93%) (48%) (13%)

Each of these figures is definitely less than the corresponding one for the free positive ion, and the diminution may represent the compensating influence of the terminal negative pole. Primary, secondary, and tertiary benzylamine and β-phenylethylamine salts give lower values than the corresponding quaternary compounds, and it is suggested [83, 84] that they also exemplify dipole action.

The above series also illustrates the diminution of the effect with distance, which, in addition, is indicated by certain observations on the nitration of sulphones ;[88] and the far stronger damping effect of the $-CH{:}CH-$ group as compared with the $-CH_2-CH_2-$ group is shown by a comparison of β-phenylnitroethane and ω-nitrostyrene :[89]



(mainly meta-.) (30% meta-.) (only traces of meta-.)

The investigation of sulphone compounds referred to above enables the compensating effect of the negative end of a dipole to be illustrated in another way. Sulphonic acids are strong electrolytes, and their anion contains, in addition to the doubly-charged sulphur atom, three equivalent, negatively charged oxygen atoms. Sulphonic esters, on the other hand, cannot undergo ionisation, and therefore contain two negatively charged oxygen atoms and a neutral oxygen atom. The removal of the alkyl group thus results in the charging of the oxygen atom to which it was attached, and the effect of increasing by this means the total compensating negative charge in the ratio 3/2 is shown in the following comparison of the

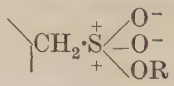
[86] A. F. Holleman and B. R. de Bruyn, *Rec. trav. chim.*, 1900, **19**, 79; *A.*, 1900, i, 481.

[87] J. W. Baker and C. K. Ingold, *J.*, 1926, 2462; **A.**, 1131.

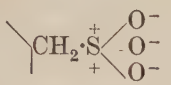
[88] R. F. Twist and S. Smiles, *J.*, 1925, **127**, 1248; *A.*, 1925, i, 902; compare C. K. Ingold, E. H. Ingold, and F. R. Shaw, *Chem. and Ind.*, 1926, **45**, 836. Compare also N. Martinet and A. Haehl, *Compt. rend.*, 1921, **173**, 775; *A.*, 1921, i, 854.

[89] B. Priebs, *Annalen*, 1884, **225**, 347; *A.*, 1885, 160.

results obtained in the nitration of a benzylsulphonic ester and the corresponding (ionised) acid :



(32% meta-.)



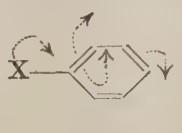
(14% meta-.)

(ii) *Theoretical Considerations.*—In view of the electrical constitution of matter, the circumstance that positive and negative poles, respectively, represent the most powerful known meta- and ortho-para-directing influences strongly suggests that *m*-orientation is associated with an attraction, and *op*-orientation with a repulsion, of certain nuclear electrons by the directing group. This consideration provides a starting point for the interpretation of older theories of the orienting action of groups.

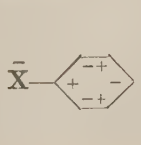
The theory of alternating residual affinity by which B. Flürscheim has with considerable success interpreted orienting effects, as well as the theory of alternately polarised atoms with which D. Vorländer, for instance, illustrated his observations, must now both be admitted to lead to certain inconsistencies. In particular, both are affected by the circumstance that, whatever may happen within the benzene ring itself, there is, in certain cases, a demonstrable absence of alternation in the side chain (compare the homologous ammonium salts and nitro-compounds). Nevertheless, both views contain many enduring features, which it is desirable to recognise beneath the different modes of expression.

The alternating affinity figure (I) for *op*-substitution, interpreted in terms of the electronic theory of valency, means that, relatively to hydrogen, the atom X allows its electrons to come more under the influence of the positive atomic nucleus of C_α, which to a corresponding extent relinquishes its control of electrons held in conjunction with C_{ortho} (II). The alternate polarity figure for the same case represents C_{ortho} as negative relatively to C_α, which it is to a greater or less degree if the adjustment mentioned has occurred (III). In formula (II), the *p*-position is reached by mutually accommodating adjustments of electrons from the two double bonds, and another method of attaining the same end is to use the conception of direct para-affinity exchange (IV); on this view a weak second-order effect might reach the *m*-position.

(I.)



(II.)

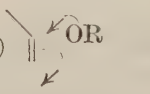


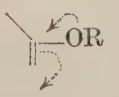
(III.)

(IV.)

The formation of residual affinities (represented by loosely-held electrons) in the *op*-positions accords with the fact that *op*-oriented substitutions are often practically instantaneous at the ordinary temperature, whilst *m*-substitutions are notoriously slow. One conception, not essentially new, of *m*-substitution is that it is a residual effect produced by the disappearance of free affinity from the *op*-positions, and this might arise from the reversal of the processes represented in (II) and (IV). This, it may be remarked, at least seems to explain why it is that in the absence of other disturbances the effect of a weak *op*-orienting group, like methyl, outweighs that of a strongly *m*-directing group, such as $-\overset{+}{N}Me_3$, in competition, and why the further substitution of a mono-substituted naphthalene (or anthraquinone) containing a *m*-directing group (NO_2, SO_3H, CN, CO_2H, etc.) in one ring always occurs in the unsubstituted nucleus.

The various series of papers in which views of this type have recently been expressed [82, 83, 87, 90] differ in the details, and the task of presenting a connected account is not without difficulties; moreover, there are many points which are quite incapable of definite determination at the present time. Thus electron shifts originating in an atom with a latent valency may be taken to represent either a momentary complete covalency displacement leading to an "active phase," or a residual valency displacement varying in amount but more or less permanently present in the molecule :

(V.) 



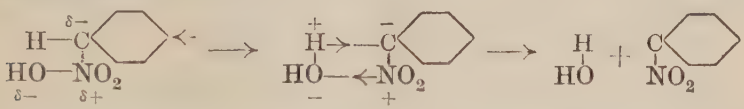
(VI.) Symbols ↘ and ↘ denote establishment of — and ···· respectively.

The evidence on this question provided by the physical properties of benzene derivatives will be considered in a later section. The other points requiring elucidation fall mainly under three headings : (*a*) the origin of the orienting influence in groups other than poles and dipoles, (*b*) the mode of transmission of the effect through the nucleus, (*c*) the mechanism of the substitution which ensues at the activated position. The remainder of this section will be devoted to a discussion of these points (taken in the reverse order) in so far as recent experiments seem to assist in their elucidation.

(iii) *Action of Substituting Agents.*—If the development of *residual* valencies in the nucleus (II or IV) is accepted, it is necessary to

[90] A. Lapworth, *J.*, 1922, **121**, 416; J. Allan, A. E. Oxford, R. Robinson, and J. C. Smith, *J.*, 1926, 401; **A.**, 397; A. W. Francis, *J. Amer. Chem. Soc.*, 1926, **48**, 1631; **A.**, 828; H. J. Lucas, *ibid.*, p. 1827; **A.**, 943; C. K. Ingold and E. H. Ingold, *J.*, 1926, 1310; **A.**, 833; C. K. Ingold and P. G. Marshall, *ibid.*, p. 3080.

assume that, after the preliminary attachment of the reagent molecule has occurred, some much more powerful factor operates and carries the process to completion by a comparatively direct route. It may be thought that the tendency of hydrion and hydroxide ion to form undissociated water will frequently provide the necessary driving force, and this view is embodied in the following symbolic expression for a nitration ($\delta+$ and $\delta-$ denote fractional charges, and the arrows the assumed directions of electron displacement) : [91]



Possibly the reason why hypochlorous acid chlorinates more easily than it oxidises aromatic compounds is that the tendency to form undissociated water from its ions is greater than the tendency to form ionising hydrogen chloride.

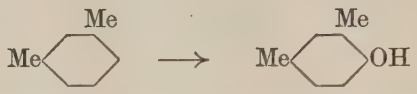
This conception assumes the prior addition of an *incipiently* ionised molecule. The alternative is to suppose [92] that a small part of the reagent is fully ionised and that the attack is by the positive ion; and it is at first sight a credible alternative because there are clear cases of nuclear attack by undoubted positive ions, for example, diazonium ions. So far as chlorination by hypochlorous acid is concerned, however, the issue has been ingeniously resolved by F. G. Soper and G. F. Smith,[93] who have shown by dynamic experiments that in the chlorination of a phenol the reaction occurs between the phenoxide *ion* and the hypochlorous acid *molecule*. The great reactivity of the phenoxide ion, as compared with molecular phenol, accords with the very strong *op*-orienting effect which would be expected to arise from the repulsion of electrons by a negative pole. That the second factor entering into the expression for the reaction velocities is the concentration of the hypochlorous acid molecule, clearly shows that this, and not the hypothetical positive chlorine ion, is the halogenating agent; for the concentration of the positive ion would be proportional ($HOCl \rightleftharpoons OH' + Cl^{\cdot}$) to that of the undissociated hypochlorous acid *divided by the hydroxyl-ion concentration* (which was varied in the experiments), so that the assumption of chlorination by the ion would lead to totally different velocity relations. It is probable [94] that similar conclusions apply to chlorination by chlorine and to other halogenations.

[91] C. K. Ingold and E. H. Ingold, *loc. cit.*

[92] Compare H. Baines, *J.*, 1922, **121**, 2810; V. Cofman, *J.*, 1919, **115**, 1040; A. W. Francis, *J. Amer. Chem. Soc.*, 1925, **47**, 2340; *A.*, 1925, i, 1261.

[93] *J.*, 1926, 1582; **A.**, 831. [94] *Idem, ibid.*

A general conception of aromatic substitution must envisage substitutions depending, not only on the dissociation of the reagent into ions, but also its separation into neutral radicals,[91] and in this connexion recent observations on the electrolytic oxidation of aromatic compounds are of considerable interest; for an anion on contact with its anode presumably becomes a neutral radical. The experiments[95] alluded to show that a so-called "negative" hydroxyl group is introduced into the nucleus in the same positions as those into which a "positive" nitro-group would enter; for instance:



This is to be expected, for the neutral hydroxyl radical (or $O{\cdot}SO_3H$ radical, if the electrolysis is in sulphuric acid) will contain one electron less than the number required to form the stable group, and will therefore seek out the negative centres of the aromatic nucleus, simulating in this respect the behaviour of a "positive" group.

(iv) *Nuclear Transmission of Orienting Effects.*—The decision between mechanisms which employ the conjugation of the Kekulé double linkings (II) and those which assume direct para-transference or shift (IV) must be separately decided in each group of cases. It is, however, germane to the general question to refer here to the contrast between the remarkable facility with which orienting influences traverse an aromatic nucleus and their apparent almost total inability to pass through even one carbon double linking situated in a side-chain.

The contrast between the almost complete inhibition of *p*-substitution in the nitration of nitrobenzene and the facility with which *o*-substitution (and *p*-substitution) takes place in ω-nitrostyrene, despite apparent analogy based on the conjugation of the systems,

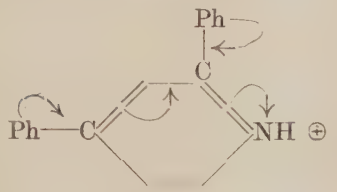
has long been recognised, and now a still more striking illustration has been provided.[96] In the nitration of 4-phenylpyridinium sulphate the effect of the pole after traversing the pyridine ring is

[95] F. Fichter and J. Meyer, *Helv. Chim. Acta*, 1925, **8**, 74; *A.*, 1925, i, 800; F. Fichter and P. Lotter, *ibid.*, p. 438; *A.*, 1925, i, 1055; F. Fichter and M. Adler, *ibid.*, 1926, **9**, 279; **A.**, 509; F. Fichter and M. Rinderspacher, *ibid.*, p. 1093.

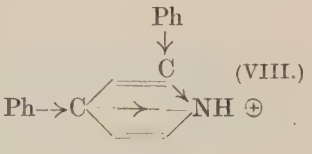
[96] R. Forsyth and F. L. Pyman, *J.*, 1926, 2912.

capable of producing a large proportion of *m*-substitution in the benzene ring (28·5% isolated out of 79·2% of identified isomerides); in the case of 2-phenylpyridinium sulphate, the meta-proportion is possibly a little higher, but certainly of the same order (34·9% isolated out of 82·3%); in the case of 3-phenylpyridinium sulphate it appears to be small (none isolated out of 64·3%). The two views of the orienting process may be expressed by formulæ (VII) and (VIII), in which the applications to the 2- and 4-phenyl compounds are represented together :

(VII.)

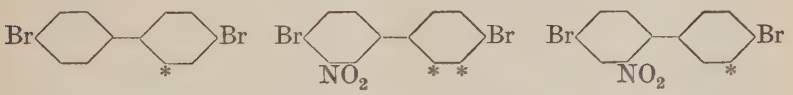


(VIII.)



and it is noteworthy that the numerical data approximately accord with anticipation based on a comparison with tertiary benzylammonium salts, Ph—C—C—$\overset{+}{N}R_2H$, using (VIII).

Further examples emerge from recent studies with diphenyl compounds.[97] *pp'*-Dibromodiphenyl nitrates mainly in the *o*-position. The prior introduction of a *m*-nitro-group in one ring causes, however, simultaneous *o*- and *m*-nitration in the other; whilst the presence of an *o*-nitro-group in one ring leads exclusively to *m*-nitration in the other (* represents the positions of substitution) :

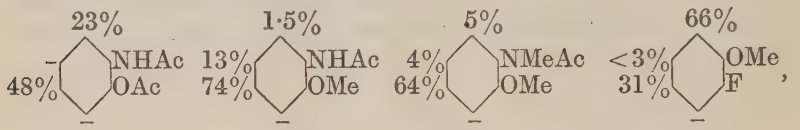


(v) *Orienting Influence of Groups.*—The orienting effects of groups which do not contain poles are naturally dominated by the constitutions of the groups.

op-*Directing groups.* It is a commonplace of orientation theories that groups attached to the nucleus by unsaturated atoms, that is, those which possess latent valencies, lead invariably to *op*-orientation in the ordinary substitution processes. For the neutral atoms N, O, F, which belong to this class and, in the combined state, contain the same number of electrons, it has been shown that the

[97] H. G. Dennett and E. E. Turner, *J.*, 1926, 476; **A.**, 390; R. J. W. Le Fèvre and E. E. Turner, *ibid.*, p. 2041; **A.**, 629. For similar but less complete studies of the nitration of diphthalylbenzidine, and of diphenyl itself, see also *idem*, *ibid.*, p. 1759; **A.**, 946; H. H. Hodgson, *ibid.*, p. 2384; **A.**, 1133; F. Bell and J. Kenyon, *ibid.*, p. 2705; **A.**, 1241.

op-orienting power runs parallel with those properties which are interpreted as indicating activity on the part of the unshared electrons; in other words, the *op*-directive power diminishes with increasing strength of the restraining nuclear charge, that is, with increasing atomic number: N>O>F. This order is inferred from the observations [98] represented by



where the figures denote the isolated or estimated proportions of the mononitro-isomerides obtained on nitration of the corresponding *o*-disubstituted compounds. The complete interpretation of such results as these involves a consideration of the disturbances which might be caused by the alkyl and acyl groups, but it may be noted at once that in the second and third examples the nitrogen atom still controls the situation despite the fact that the distribution of alkyl and acyl groups is such as to handicap its action.

Alkyl groups contain no unshared electrons; they nevertheless promote *op*-substitution, although not very powerfully, and substitution of the same type occurs if the carbon atom adjoining the ring is replaced by a tetracovalent silicon or tin atom.[99] There is reason to think that these atoms allow their shared electrons to be controlled by the nucleus of an attached carbon atom to a greater extent than would hydrogen in a similar situation.[99a] At any rate, this general statement seems to accord with the effect of replacing hydrogen by alkyl in composite groups, when an increase in the *op*-orienting influence (or diminution in the *m*-directing influence) of the entire group takes place. This is interpreted in accordance with G. N. Lewis's electron-displacement mechanism and is well illustrated by the nitrations of benzoic esters: [1]

$C_6H_5 \cdot CO_2H$	$C_6H_5 \cdot CO_2Me$	$C_6H_5 \cdot CO_2Et$
(*m*-, 80·2%.)[2]	(*m*-, 73·2%.)	(*m*-, 68·4%.)

[98] C. K. Ingold and E. H. Ingold, *J.*, 1926, 1310; **A.**, 833; E. L. Holmes and C. K. Ingold, *ibid.*, p. 1328; **A.**, 831.

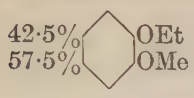
[99] D. Vorländer, K. Kunze, and E. Schroedter, *Ber.*, 1925, **58**, 1900; *A.*, 1925, i, 1255.

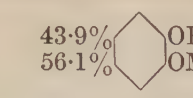
[99a] H. J. Lucas and H. W. Moyse, *J. Amer. Chem. Soc.*, 1925, **47**, 1459; *A.*, 1925, i, 770; H. J. Lucas, T. P. Simpson, and J. M. Carter, *ibid.*, p. 1462; *A.*, 1925, i, 766.

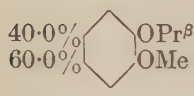
[1] A. F. Holleman, *Rec. trav. chim.*, 1899, **18**, 267.

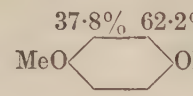
[2] Probably the true value for the *un-ionised* carboxyl group is slightly higher.

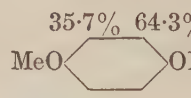
and mixed pyrocatechol and quinol ethers : [3]





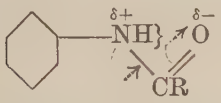


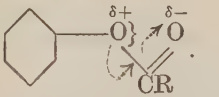




In the last two series, the order of the effects of the ethoxy- and *n*-propoxy-groups is not the same, and the investigators attribute this to the distribution over the molecule of a considerable proportion of the effect of the larger alkyl group.

The opposite influence of acyl groups, namely, the enhancement of *m*-orienting and the weakening of *op*-orienting effects, has long been recognised, and is familiarly illustrated by the fact that substitutions in *o*- and *p*-alkyloxyphenyl esters are controlled by the alkyloxy-group. The effect may be consistently interpreted as the result of a partial appropriation of electrons by the carbonyl oxygen atom; this confers partial dipolar (betaine) character on the carboxyl and carboxylamide groups, and in phenyl esters the small positive charge next the nucleus, although it may not be strong enough to bring about *m*-substitution, will oppose the *op*-orienting movement of the lone electrons :





Many more or less complex illustrations of this phenomenon are available, but some particularly striking examples in which the effect is enhanced by the use of bivalent acyl groups, like succinyl, have recently been published.[4] Under conditions in which succinanil, phthalanil, etc., yield mainly *p*-nitro-derivatives, the corresponding *p*-tolils substitute to the extent of 76—84% in the position indicated :

R_2 = { Succinyl, phthalyl, 3-nitrophthalyl, tetrachlorophthalyl.

As the authors remark, the bivalent acyl radical " does not sufficiently influence the amino-group to enable *m*-substitution to occur, but it so reduces its directive influence in the case of *p*-toluidine as

[3] J. Allan, A. E. Oxford, R. Robinson, and J. C. Smith, *J.*, 1926, 401; **A.**, 397.

[4] O. L. Brady, W. G. E. Quick, and W. F. Welling, *J.*, 1925, **127**, 2264; *A.*, 1925, i, 1400.

to enable the comparatively feebly directive methyl group to take control."

m-*Directing groups.* The halogens are recognised from the stability of their ions and other evidence to be elements of high electron-affinity, and the consideration of such a series as

$C_6H_5\cdot CH_2Cl$ (meta-, 4%.) $C_6H_5\cdot CHCl_2$ (meta-, 35%.) $C_6H_5\cdot CCl_3$ (meta-, 64%.) } (for nitration)

shows that the introduction of each halogen atom independently operates in favour of *m*-substitution. The action, in fact, is the opposite of that associated with alkyl groups, and the contrast has been illustrated [87] by the introduction of methyl and bromine in place of the hydrogen atoms of the rather strongly *m*-orienting group $-CH_2\cdot NO_2$:

$C_6H_5\cdot C(CH_3)_2\cdot NO_2$ (meta-, 29%.) $C_6H_5\cdot CH_2\cdot NO_2$ (meta-, 50%.) $C_6H_5\cdot CBr_2\cdot NO_2$ (meta-, 84%.)

In these cases, the sharing of the lone halogen electrons with the attached atom is impossible without disruption of the molecule, and in chlorobenzene, etc., where the sharing process can, and presumably does, occur (leading to *op*-substitution), it may be supposed that there is a simultaneous attraction towards the halogen nucleus of *all* its electrons, shared and unshared, weakening the *op*-orienting effect. Probably two simultaneous effects, $\curvearrowright\!\!\rightarrow Cl$, which may be termed "tautomeric," $\curvearrowright$), and "inductive," $\rightarrow$, would be propagated by different paths in the nucleus, and it is doubtless in this direction, amongst others, that the explanation of many obscure phenomena, for instance the *o*-/*p*- ratio, is to be sought. In the carbonyl group and similar groups, there will be a shifting of electrons towards the more electronegative element and the tautomeric and inductive effects will collaborate, $Ph\curvearrowright\!\!\rightarrow CO$. In the amidine salt group, the effect of a positive pole is superimposed in addition; accordingly benzamidine nitrates almost wholly in the *m*-position.[5]

The o-/p-*ratio.* One is reminded of the problem of the *o*-/*p*-ratio by the recent re-investigation of the nitration product of benzil, which contains *mm'*-, *om'*-, and *oo'*-derivatives (70%, 20%, and 10%, respectively) but no considerable quantity of *p*-substituted isomerides.[6] Amongst the *m*-orienting groups, the rule seems to be

[5] R. Forsyth, V. K. Nimkar, and F. L. Pyman, *J.*, 1926, 800; **A.**, 611.
[6] F. D. Chattaway and E. A. Coulson, *ibid.*, 1070; **A.**, 728.

that those with a real double bond similar to that in benzoyl compounds give mainly *o*-by-products, whilst those composed wholly of single (or semipolar double) bonds yield *p*-products in greater quantity. These and other regularities of a like kind may be partly collated (probably steric hindrance and the varying electron-seeking tendencies of different reagents are also factors) by supposing that tautomeric disturbances reach the para-position more easily than the ortho-, whilst with inductive disturbances, which are generally weaker, the reverse is the case. Using T and I for the two types of disturbance, and + and − for promoting and impeding effects, the different cases may be tabulated :

(i) $+I = o>p$ (toluene).
(ii) $-I = p>o$ (phenyl- and benzyl-ammonium salts, benzenesulphonic acid, benzotrichloride).
(iii) $-T-I = o>p$ (benzoyl compounds, nitrobenzene).
(iv) $+T-I = p>o$ (halogenobenzenes, phthalanil).

The spatial factor seems to be present in the predominating *p*-nitration of *tert.*-butylbenzene,[7] and the effect of varying the reagent is well brought out by recent studies on the mercuration of toluene and nitrobenzene.[8] Comparison of the results with those obtained for nitration [86] is instructive :

Nitration of nitrobenzene	*o*	6·4%	Mercuration of nitrobenzene	*o*	52·6%
	m	93·2%		*m*	38·5%
	p	0·4%		*p*	8·9%

The observations are, of course, on a footing with the well-known predominating *o*-mercuration of benzoyl compounds. In the mercuration of these compounds, as in their nitration, the quantity of *o*-by-product exceeds the quantity of *p*- ; the noteworthy feature is that in mercuration the quantities of ortho- and para- taken together exceed that of the meta-derivative. A considerable amount of substitution in the position adjacent to the nitro-group also takes place in the mercuration of the three nitrotoluenes.[9]

In view of its possible connexion with the subject, reference may be made to H. Wieland and H. Jung's discovery [10] that the long-known product of the oxidation of trinitroresorcinol with bromine

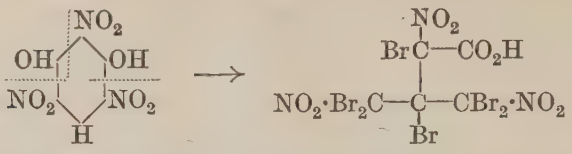
[7] D. F. du T. Malherbe, *Ber.*, 1919, **52**, 319; *A.*, 1919, i, 261.

[8] S. Coffey, *J.*, 1925, **127**, 1029; O. Dimröth, *Annalen*, 1925, **446**, 148; **A.**, 1926, 312; J. Jürgens, *Rec. trav. chim.*, 1926, **45**, 61; **A.**, 312. Compare A. F. Holleman, *Rec. trav. chim.*, 1923, **42**, 355.

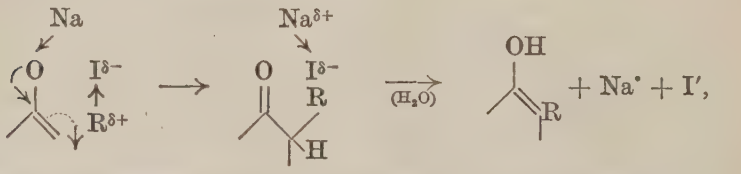
[9] S. Coffey, *J.*, 1926, 637; **A.**, 628; *ibid.*, p. 3215; H. Burton, F. Hammond, and J. Kenner, *ibid.*, p. 1802; **A.**, 966.

[10] *Annalen*, 1925, **445**, 82; *A.*, 1925, i, 1374.

water is a derivative of *iso*valeric acid, in the formation of which *p*-carbon atoms have become united :



Special Mechanisms.—Doubtless there are many substitutions in which special mechanisms determine a particular type of result; in such cases, either the circumstances of the reaction or collateral evidence of some other kind should indicate, if it does not elucidate, the cause of the anomaly. An interesting example is furnished by recent work on the nuclear alkylation of phenols, through their salts, in non-ionising solvents (benzene, toluene) by alkyl halides, which, when ionising solvents (methyl and ethyl alcohols) are employed, cause exclusive substitution on oxygen.[11] In these nuclear alkylations, the substituent invariably enters the ortho-position, even although the para-position may be unoccupied. The relevant circumstances are, first, that the reaction occurs only in non-dissociating media, and secondly, that only reactive, readily hydrolysable, alkyl halides can be used. This suggests, first, that the reaction is one which requires the presence, not of the phenoxide ion, but of the undissociated metallic salt,[12] and, secondly, that the incipient intramolecular ionisation of the alkyl halide must exceed a certain necessary minimum. Both points are incorporated in the scheme :

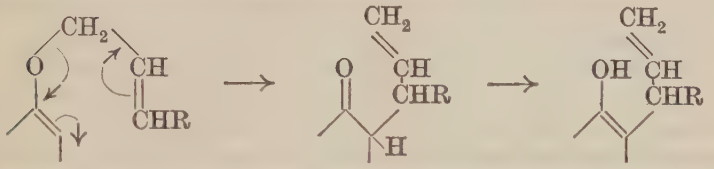


and the possibility of a cyclic mechanism is clearly established by the related rearrangements of aryl allyl ethers, in which the allyl group migrates to the ring. That these reactions are actually analogous is

[11] L. Claisen, *Z. angew Chem.*, 1923, **36**, 478; *A.*, 1923, i, 1094; *idem*, D.R.-P. 412169; *A.*, 1925, i, 1410; L. Claisen, F. Kremers, F. Roth, and E. Tietze, *Annalen*, 1925, **442**, 210; *A.*, 1925, i, 656; L. Claisen and E. Tietze, *ibid.*, 1926, **449**, 81; **A.**, 1034.

[12] The existence of undissociated salts (*e.g.*, sodium iodide) in feebly ionising organic solvents can probably be inferred from the fact that such solutions, according to measurements of conductivity, appear to conform to the requirements of the law of mass action within wide limits (Professor H. M. Dawson, private communication).

plainly indicated by the fact that here again the group enters only the ortho-position even when the para-position is unoccupied. In these cases, however, the cyclic mechanism may be demonstrated [13] by the use of a γ-substituted allyl group, which becomes an α-substituted allyl group in the product of the rearrangement :



Note.—A considerable body of work has recently been carried out on the replacement of atoms and groups other than hydrogen, and on the influence of substituents on the reactivity of atoms and groups situated in another side-chain; limitations of space render it desirable to postpone reporting on these two important branches of the general theme.

Physical Properties of Benzene Derivatives.

Some interesting parallelisms have been drawn between the effect of the presence of a group in an aromatic compound on its melting point, boiling point, and dielectric constant, on the one hand, and the orienting influence of the group, on the other. Such comparisons are instructive because they indicate that directive influence is to a considerable extent a permanent specific property of the molecule and not merely a temporary factor brought into play only at the moment of reaction through some " activation " process.

Melting Point and Boiling Point.—A. W. Francis, D. H. Andrews, and J. Johnston [14] point out that if a series of monosubstituted benzenes, C_6H_5X, are arranged in accordance with Holleman's series for diminishing *op*-orienting power and increasing *m*-orienting power, the m. p.'s and b. p.'s fall through the *op*-series and rise through the *m*-series; and a similar relation exists for compounds of the type HX :

	op-Orienting.						*m*-Orienting.			
X =	OH	NH_2	Br	Cl	CH_3	H	CHO	NO_2	SO_3H	CO_2H
C_6H_5X.										
M. p.	42°	−6°	−31°	−45°	−94°	5°	−13°	5°	66°	121°
B. p.	183°	184°	156°	132°	110°	80°	179°	210°	—	249°
HX.										
M. p.	0°	−77°	−87°	−112°	−184°	−259°	—	—	—	9°
B. p.	100°	−39°	−69°	− 83°	−153°	−258°	−21°	—	—	101°

[13] L. Claisen and E. Tietze, *Ber.*, 1925, **58**, 275; *A.*, 1925, i, 389; *ibid.*, 1926, **59**, 2344; **A.**, 1241.

[14] *J. Amer. Chem. Soc.*, 1926, **48**, 1624; **A.**, 828.

The correspondence, although striking, is obviously imperfect; thus the order chosen for the orienting action of NO_2 and CO_2H is not that which would be deduced from the relative proportions of *m*-derivative given by nitrobenzene and benzoic acid on nitration; and, again, the position given to $OH(>NH_2)$ is probably based on substitution reactions (*e.g.*, aqueous bromination) in which the real orienting group is not –OH but the pole $-O^{\odot}$ (p. 135).

Turning to disubstituted benzenes, C_6H_4XY, the same workers, and also I. A. Pastak,[15] direct attention to a general rule governing the relative melting points of *o*-, *m*-, and *p*-isomerides. It is that, whereas the *p*-compound has the highest m. p., of the other two isomerides that in which the groups co-operate in their directive effect has the lowest m. p. Both parts of the rule are violated, for example, by the chlorobenzaldehydes, in which the m. p. sequence is $o>p>m$ instead of $p>m>o$; nevertheless it appears to hold good in about 70—80% of the available examples.

Such rules as these, even when they may not be perfectly obeyed, clearly point to the *existence* of a connexion, however indirect, between the properties under comparison, and it will be agreed that "any indication may be valuable in a field in which so little is known definitely."

Dielectric Constant.—In the same paper, Francis, Andrews, and Johnston direct attention to an approximate regularity in the dielectric constants of the monosubstituted benzenes represented in the table above. Like the m. p.'s and b. p.'s, these constants fall from phenol to toluene and rise from benzene to nitrobenzene provided that we except chlorobenzene, the constant of which is higher than that of phenol. Similar approximate relations between the dielectric constant and orienting properties of compounds have been pointed out previously.[16]

The interest which at present centres around the dielectric constant, however, arises from the fact that a theory [17] has been provided whereby it is possible to trace the connexion between the constant and certain definite structural properties of the molecule.[18] It is necessary to consider the chain of reasoning briefly in order to bring out the power, and the present limitations, of the method as a means of elucidation of molecular structure.

[15] *J. Chim. phys.*, 1925, **22**, 48, 264; *A.*, 1925, i, 531; ii, 759.

[16] H. G. Rule, *J.*, 1924, **125**, 1121; H. G. Rule and T. R. Patterson, *ibid.*, p. 2155.

[17] P. Debye, *Physikal. Z.*, 1912, **13**, 97; J. J. Thomson, *Phil. Mag.*, 1914, **27**, 757; *A.*, 1914, ii, 450; C. P. Smyth, *ibid.*, 1923, **45**, 849; 1924, **47**, 530; *J. Amer. Chem. Soc.*, 1924, **46**, 2151; *A.*, 1924, ii, 810; R. Gans, *Ann. Physik*, 1921, **64**, 481.

[18] Compare G. N. Lewis, "Valency and the Structure of Atoms and Molecules" (1923).

If in a molecule the mean electrical centre (analogous to centre of gravity) of all the electrons and the corresponding centre of all the positive atomic nuclei do not coincide, the molecule as a whole will be equivalent to a dipole and will possess a definite electric moment (μ). In the presence of an electric field, such molecules will tend to orient themselves in the direction of the field; but this tendency will be opposed by thermal agitation, with the result that there will arise a statistical average degree of alinement depending on the temperature. The molecular fields thus reinforce the exciting field passing through the substance. The moments of the oriented dipoles will, however, be greater than in the undisturbed condition, because the field itself will create a further intramolecular separation of $\pm$ charges in the same direction until the effect of the whole field (original + induced) is just balanced by the restoring forces. The gross increase in the field (determining the dielectric constant ε) thus depends on the sum of two terms, one of which (the orientation-polarisation, P_μ) represents the contribution, limited by temperature, of the oriented dipoles, whilst the other ($P_E + P_A$) denotes the effect of the additional electrical separation as limited by the "rigidity" ("Bindungsfestigkeit") of the charges. The latter term is divided into two parts, P_A and P_E, because one can be evaluated more easily than the other; for the part depending on the displacements of the relatively very light electrons (the electron-polarisation, P_E) is the only part which contributes to the "dielectric constant" (*i.e.*, the square of the refractive index, n) in the rapidly oscillating electric fields of visible light. The other part (the atom-polarisation, P_A), which arises from the relative displacements of the comparatively heavy atomic nuclei, can only be evaluated *directly* if the appropriate optical data for the far infra-red region (slower electrical oscillations) are available; its chemical interest is, however, just as great as that of the dipole moment, since it also measures a specific molecular property, namely, the tendency towards incipient division into ions.

Debye's equation (modified),

$$\frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{M}{d} = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} + P_A + \frac{4\pi N}{9kT}\mu^2,$$

k = Boltzmann's gas constant. N = Avogadro's number.

which, in accordance with the above summary may be abbreviated to $P = P_E + P_A + P_\mu$, applies primarily to vapours, but with suitable modification is also applicable to dilute solutions in an appropriate solvent. Its application to strong solutions and pure liquids having dipolar molecules is not so good owing to intermolecular action, especially "dipole association," $\overset{+}{-}\!\!=\!\!\overset{-}{+}$, which tends

to lower the value of ε.[19] It remains to be added that in equating P_E to the Lorentz expression $[R_L]$ a wave-length in the red region is chosen, since, for a colourless substance, this is sufficiently far from the (ultra-violet) frequency of the resonating electrons to render negligible the omitted correction for dispersion; the correction factor $(1 - \lambda_0^2/\lambda^2)$ can, however, be applied if necessary. Similarly $P_A + P_E$ can be equated to $[R_L]_{\text{infra-red}}$ only if the refractive index is taken well beyond the infra-red bands due to the vibrating atoms.

The Dipole Moment and Atom-polarisation of Benzene.—Recently-determined values for the dielectric constant,[20] refraction, and dispersion of benzene in the liquid state near the ordinary temperature give $P = 26{\cdot}5$ and $P_E = 25{\cdot}7$. Since $P = P_E + P_A + P_{\mu(\text{liq.})}$, it follows that $P_A + P_{\mu(\text{liq.})}$ has the small value 0·8, and there are two indirect reasons for inferring that the whole of this is to be laid to the account of atom polarisation. First, similar small values of $P_A + P_{\mu(\text{liq.})}$ are invariably observed in very diverse types of molecules provided that their projections on three space-axes are *symmetrical* (marked *) : [21]

$P_A + P_{\mu(\text{liq.})}$	CCl_4.* 3·7	$CHCl_3$. 23·9	CH_4.* 0·6	$CH_3 \cdot NO_2$. 37·4	$C(NO_2)_4$.* 1·1
	p-xylene.*	*m*-xylene.	*o*-xylene.	mesitylene.*	$Ni(CO)_4$.*
$P_A + P_{\mu(\text{liq.})}$	1·3	4·0	7·0	1·5	2·1
	Cl—C—H ‖ Cl—C—H	H—C—Cl* ‖ Cl—C—H	Cl—C—Cl ‖ H—C—H	Br—C—H ‖ Br—C—H	Br—C—H* ‖ H—C—Br
$P_A + P_{\mu(\text{liq.})}$	34·6[5]	2·7	23·6	27·6	3·9

Secondly, in the *solid* state there can be no free orientation of the molecules ($P_\mu = 0$) and therefore dipole substances should show a diminution in the dielectric constant when frozen. This is well illustrated in the case of water, for which P drops 8 units on freezing :

$$P_{(\text{liq.})} = P_E + P_A + P_{\mu(\text{liq.})} = 17{\cdot}5;\ P_E = 3{\cdot}7;\ \therefore\ P_A + P_{\mu(\text{liq.})} = 13{\cdot}8.$$
$$P_{(\text{sol.})} = P_E + P_A = 9{\cdot}5;\ P_E = 3{\cdot}7;\ \therefore\ P_A = 5{\cdot}8.$$

Here the approximate value of the refractive index in the far infra-red is known ($n^2 = 4$) and the derived estimates $P_E + P_A = 9$ and $P_A = 5{\cdot}3$ are in good agreement. In the case of benzene, however, there is no diminution in P on passing from the liquid to the solid, but, on the contrary, a very small increase ($P_{(\text{liq.})}$ 26·5; $P_{(\text{sol.})}$ 26·9). A similar behaviour is shown by the symmetrical substance carbon tetrachloride.[21]

[19] L. Ebert, *Z. physikal. Chem.*, 1924, **113**, 1; *A.*, 1925, ii, 14; *ibid.*, 1925, **114**, 430; *A.*, 1925, ii, 262.

[20] W. Graffunder, *Ann. Physik*, 1923, **70**, 225.

[21] L. Ebert, *loc. cit.*; J. Errera, *J. Phys. Radium*, 1925, **6**, 390; **A.**, 1926, 225.

An elaborate theoretical investigation has led R. Sänger [22] to the conclusion that the dipole moment of benzene is probably zero, and it is of interest to compare the corresponding estimate of its atom-polarisation (0·8) with that of a typical ionising substance such as water (5·8).

The Dipole Moment of Benzene Substitution Products.—A variety of circumstances points to the conclusion that dipole moment is a property of groups.[23] The following data for benzene homologues

C_6H_5X ..... X =	Me.	Et.	Pr$^{\alpha}$.	Pr$^{\beta}$.	Bu^{iso}.
$P_A + P_{\mu(\text{liq.})}$	2·9	3·4	3·0	3·5	3·0

apply to the liquid state, in which the polar orientation is imperfect; nevertheless the approximate constancy of the values clearly shows that both the atom-polarisation in the aliphatic side-chain and the effect of all the carbon atoms *after the first* on molecular dipole moment are inappreciable. On contrasting these results with the following series (which relate to the vapour—free polar orientation),

R·OH { R =	H.	Me.	Et.
$P_A + P_\mu$ =	56·3	54·7	54·9

it becomes evident that an effect of the hydroxyl group is now under observation; and, since the values of P_A for hydrocarbons and even for water are small in comparison with *these* observed values for $P_A + P_\mu$, by far the greater part of them must be attributed to P_μ, which is therefore sensibly constant in the three compounds.

The smallness of P_A for many classes of compounds renders it possible, as an approximation, to neglect it in comparison with P_μ for definitely dipolar molecules, and to calculate the dipole moment of the individual molecule (μ) from the approximate equation $P - P_E = 4\pi N\mu^2/9kT$. An interesting and important series of data [24] relating to benzene derivatives has been treated in this way. The values of μ for some monosubstituted benzenes are as follows :

C_6H_5X { X =	CH_3.	Br.	Cl.	NO_2.	NMe_2.
μ =	0·43	1·56	1·58	3·75	$1·39 \times 10^{-18}$ E.S.U.

From these data alone it is, of course, impossible to tell in which direction the charges are distributed as between the group and the nucleus; but, as Sir J. J. Thomson pointed out,[25] the electric moment of a polysubstituted benzene should be the vector sum of the

[22] *Physikal. Z.*, 1926, **27**, 165; **A.**, 456.

[23] L. Ebert, *loc. cit.*; C. P. Smyth, *loc. cit.*

[24] K. Höjendahl, *Nature*, 1926, **117**, 896; **A.**, 779. The dielectric constants were determined in benzene solution (non-dipolar solvent) and extrapolated to infinite dilution in order to eliminate the effect of dipole association.

[25] *Phil. Mag.*, 1923, **46**, 513; *A.*, 1923, ii, 682.

moments due to the groups, provided that these groups act independently and that the hexagonal symmetry of the ring is not distorted by substitution. It follows that the investigation of disubstituted benzenes must reveal the relative signs of the component effects; thus the moment of *p*-nitrotoluene should be the *sum* of the moments of toluene and nitrobenzene if, and only if, the two groups cause an *unlike* displacement of $\pm$ charges when attached separately to the nucleus. In the following table, the experimental values of the molecular dipole moment, μ, for a number of polysubstituted benzenes are compared with the values calculated by compounding the moments (above table) due to the separate groups :

Substance.	μ (obs.).	μ (calc.).	Formula (a and b from previous table).
o-Dinitrobenzene ...	$5{\cdot}95 \times 10^{-18}$	$6{\cdot}50 \times 10^{-18}$	$\sqrt{a^2 + a^2 + 2a^2 \cos 60^\circ} = \sqrt{3}a$
m- ,, ...	4·02	3·75	$\sqrt{a^2 + a^2 + 2a^2 \cos 120^\circ} = a$
p- ,, ...	0·8	0·00	Zero from symmetry.
s-Tribromobenzene	0·3	0·00	Zero from symmetry.
o-Nitrotoluene	3·56	3·62	$\sqrt{a^2 + b^2 - 2ab \cos 60^\circ}$
p- ,, ...	4·30	4·18	$\sqrt{a^2 + b^2 - 2ab \cos 180^\circ} = a + b$
o-Chloronitrobenzene	4·25	4·75	$\sqrt{a^2 + b^2 + 2ab \cos 60^\circ}$
m- ,,	3·38	3·27	$\sqrt{a^2 + b^2 + 2ab \cos 120^\circ}$
p- ,,	2·52	2·17	$\sqrt{a^2 + b^2 + 2ab \cos 180^\circ} = a - b$
p-Bromonitrobenzene	2·69	2·19	$\sqrt{a^2 + b^2 + 2ab \cos 180^\circ} = a - b$

Perfect agreement is not to be expected, because, as the values for tribromobenzene and *p*-dinitrobenzene show, atom-polarisation is not negligible; also the assumptions made in compounding the vectors are probably only approximately fulfilled. Nevertheless, the results show clearly that the dipoles due to NO_2, Cl, and Br are of the same sign, whilst that due to Me is of the opposite sign. Since the dipole due to NO_2 must be in the direction of its semipolar double linking, these results may be taken as establishing permanent electron shifts in the directions :

$$\overleftarrow{}\ C_6H_5{\cdot}Me \qquad \overrightarrow{}\ C_6H_5{\cdot}Hal \qquad \overrightarrow{}\ C_6H_5{\cdot}NO_2$$

These are the directions deduced for the *inductive* displacement from aromatic substitution data, and it is of considerable interest that the same results, supplemented by those of another worker,[26] lead to the sequence

$$\overset{\text{repulsion}}{\overleftarrow{}}\ \overset{\text{electron attraction}}{\overrightarrow{}}$$
$$Me > H < I < Br < Cl < NO_2$$

which is also in agreement with expectation based on orientation

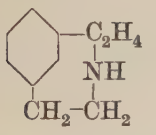
[26] J. Errera, *Compt. rend.*, 1926, **182**, 1623; **A.**, 779.

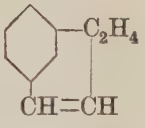
reactions. Part of the large moment of nitrobenzene is, of course, due to the dipolar constitution of the nitro-group itself.

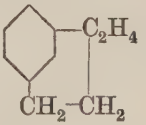
It follows from the sequences N>O>Hal and Hal>O>N deduced for tautomeric electron-repulsion and inductive electron-attraction in oriented substitutions that the first effect is at a maximum and the second at a minimum for N; hence, when the sign of the dipole in dimethylaniline has been determined, it should be possible definitely to answer the question whether tautomeric, like inductive, effects are associated with a permanent displacement of the electrons.

Concluding Notes.—The Reporter is more than usually conscious of the fact that the foregoing account is far from representative of the different types of work falling within the Homocyclic Division of Organic Chemistry which have signalised the year under review, and one of the most serious omissions relates to the study of natural products in which noteworthy advances (apart from those connected with muscone and civetone) have been made, including the complete elucidation, by analytical methods and synthesis, of the constitution of thyroxine. This important investigation, however, is being dealt with in the Biochemical section of these Reports, and partly on this account, and partly because the space which has been occupied is already too great, it seems desirable to leave the general topic of natural products to be dealt with on a future occasion.

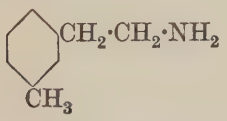
It should also be mentioned that the supposed "meta-ring" compounds

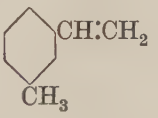


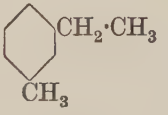




discussed in the Annual Reports for 1920 (p. 73) have now been shown to possess different constitutions : [27]







C. K. Ingold.

[27] A. F. Titley, *J.*, 1926, 508; **A.**, 512.

Part III.—Heterocyclic Division.

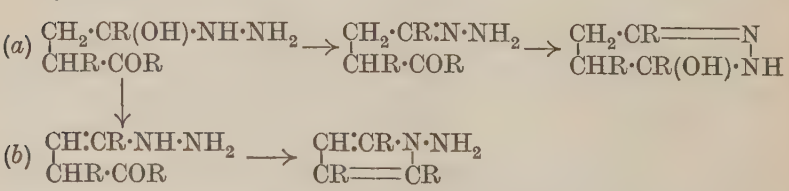
Pyrrole Derivatives.

T. M. Lowry [1] has pointed out that the nitrogen atom in the pyrrolidine nucleus of the nicotinium ion must be regarded as asymmetric, a view supported by the fact that, like some other alkaloids, nicotine changes its sign of rotation on conversion into a salt, for example, nicotine $[\alpha]_D$ −169°; nicotine acetate, $[\alpha]_D$ +18·8°. In the course of a paper mainly concerned with the configuration of certain amino-acids exhibiting dextrorotation, P. Karrer, K. Escher, and (Mlle.) R. Widmer [2] conclude that *l*-proline, *l*-hygric acid and *l*-stachydrine must belong to a group the configuration of which is typically represented by *l*-asparagine. The group includes *d*-glutamic acid, *d*-glutamine, *d*-ornithine, and *d*-lysine, and they suggest that these natural constituents of protein, as well as some of the simpler alkaloids, such as nicotine, possess a uniform configuration.

G. Korschun and (Mme.) C. Roll [3] are of opinion that the first stage in the action of hydrazine on αδ-diketones is the direct addition of one molecule of the reagent, after which elimination of water may occur in either of two ways :

(*a*) elimination of imino-hydrogen with hydroxyl, followed by ring closure to a 1 : 2-diazine.

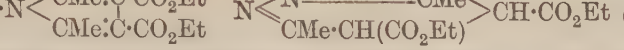
(*b*) a hydrogen atom of the methylene group is eliminated with the hydroxyl group, followed by ring closure to an aminopyrrole.



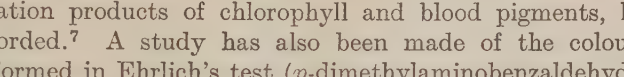
The relative mobilities of the hydrogen atoms, which depend on the nature of the substituents and the conditions, especially the temperature, determine which reaction will take place. On this view of the mechanism, the heats of formation of an aminopyrrole and the isomeric 1 : 2-diazine should be approximately the same, and this has been found to be the case for ethyl 1-amino-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate (I), 1566·8 cal., and ethyl 3 : 6-di-

[1] *Nature*, 1926, **117**, 417; **A.**, 338.
[2] *Helv. Chim. Acta*, 1926, **9**, 301; **A.**, 505.
[3] *Bull. Soc. chim.*, 1926, [iv], **39**, 1223; **A.**, 1154.

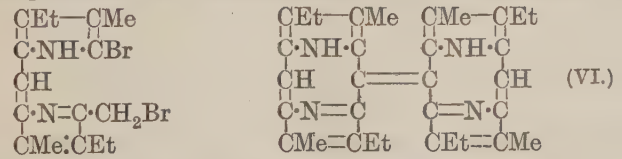
methyl-4 : 5-dihydro-1 : 2-diazine-4 : 5-dicarboxylate (II), 1588·2 cal.[4]



Syntheses of many simple and complex pyrroles have been described by H. Fischer and his co-workers chiefly by methods referred to in previous Reports.[5] Pyrryl ketones have been successfully prepared by the Friedel-Crafts process, both with aryl and with alkyl radicals,[6] and new syntheses of cryptopyrrole (2 : 4-dimethyl-3-ethylpyrrole) and of xanthopyrrolecarboxylic acid, both important disintegration products of chlorophyll and blood pigments, have been recorded.[7] A study has also been made of the colouring matters formed in Ehrlich's test (*p*-dimethylaminobenzaldehyde in hydrochloric acid).[8] Thus ethyl β-5-carbethoxy-2 : 4-dimethyl-3-pyrrylmethylmalonate (III) gives the deep-violet coloured ethyl β-5-*p*-dimethylaminobenzylidene-2 : 4-dimethyl-3-pyrrylmethylmalonate (IV).



Aetioporphyrin and the corresponding aetiohæmin and aetiophyllin were isolated by Willstätter in 1913 as the parent substances of a number of proximate degradation products of chlorophylls and hæmoporphyrins and have since been prepared from porphyrins from other sources. Aetioporphyrin is therefore an important product in these difficult and complex investigations and its synthesis by H. Fischer and J. Klarer [9] is of considerable interest both to the biologist and to the chemist. Cryptopyrrole (2 : 4-dimethyl-3-ethylpyrrole), on bromination in cold acetic acid, yields a compound, $C_{16}H_{20}N_2Br_2$, believed to be represented by (V), which is converted



[4] A. Gounder and (Mme.) C. Roll, *ibid.*, p. 1222; **A.**, 1155.

[5] 1923, **20**, 136; 1924, **21**, 124; 1925, **22**, 133, and *Annalen*, 1926, **450**, 109; **A.**, 1256.

[6] H. Fischer and F. Schubert, *Z. physiol. Chem.*, 1926, **155**, 99; **A.**, 737.

[7] With B. Walach, *Ber.*, 1925, **58**, 2818; **A.**, 1926, 178; with J. Klarer, *Annalen*, 1926, **447**, 48; **A.**, 412.

[8] With C. Nenitzescu, *Z. physiol. Chem.*, 1925, **145**, 295; **A.**, 1926, 178.

[9] *Annalen*, 1926, **448**, 178; **450**, 181; **A.**, 962, 1261; compare H. Fischer and B. Walach, *ibid.*, 1926, **450**, 164; **A.**, 1261.

by sulphuric acid into a substance (VI) indistinguishable in crystallographic characters, absorption spectrum, and solubility from Willstätter's aetioporphyrin. With ferric chloride, it gives the corresponding aetiohæmin and with magnesia and potassium hydroxide in methyl alcohol the appropriate aetiophyllin. An isomeric substance, *iso*aetioporphyrin, has also been obtained,[10] as well as other substances of this series.[11] The name " porphin " is suggested for the parent substance of this type free from β-substituents and efforts are now being made to synthesise it.

Indole and Allied Substances.

Work in this group has been, as usual, largely concerned with problems bearing on the constitution of natural products or their synthetic analogues, but a few observations on the primary materials have been made. J. van der Lee [12] suggests that in Nenitzescu's [13] preparation of indole by the reduction of *o*ω-dinitrostyrene with iron filings and acetic acid, in which a yield of 30% is claimed, the intermediate products must be *o*ω-diaminostyrene and *o*-aminophenylacetaldehyde.

In continuation of work on the now well-known transition of indole to quinoline, G. Heller and collaborators [14] have shown that, although the main product of the action of diazomethane on isatin is 2 : 3-dihydroxyquinoline, some 3 : 4-dihydroxy*iso*quinoline is also formed. 5-Chloro- and 5-bromo-isatins furnish the corresponding 2 : 3-diketotetrahydroquinolines with the halogen in each case in the 6-position.

E. C. Kendall, A. E. Osterberg, and B. F. MacKenzie,[15] in attempting the synthesis of substances with formulæ akin to that supposed by the same authors to represent the constitution of thyroxine, have prepared an interesting series of complex indole derivatives, but the main object of this work has become of secondary importance in view of Harington's [16] demonstration that this hormone is not heterocyclic in structure.

W. H. Perkin and L. Rubenstein [17] found great difficulty in the preparation and use of phenylhydrazines of the type

$$(MeO)_2C_6H_3\cdot NH\cdot NH_2$$

[10] H. Fischer and P. Halbig, *Annalen*, 1926, **448**, 193; 1926, **450**, 151; **A.**, 963, 1256.

[11] H. Fischer and others, *ibid.*, pp. 132, 201; **A.**, 1256, 1261.

[12] *Rec. trav. chim.*, 1925, **44**, 1089; **A.**, 1926, 179.

[13] *Ber.*, 1925, **58**, 1063; *A.*, 1925, i, 973.

[14] *Ibid.*, 1926, **59**, 704; **A.**, 620.

[15] *J. Amer. Chem. Soc.*, 1926, **48**, 1384; **A.**, 734; compare L. Kalb and co-workers, *Ber.*, 1926, **59**, 1858, 1860; **A.**, 1151, 1152.

[16] *Biochem. J.*, 1926, **20**, 293, 300; **A.**, 644, 724.

[17] *J.*, 1926, 357.

required for the production of a series of dimethoxyindoles to be used for conversion into carbolines and diazines related to harmine and harmaline. The 2 : 5- and 3 : 4-dimethoxyphenylhydrazines were, however, obtained, of which the latter, by condensation with (*a*) *cyclo*hexanone and (*b*) ethyl pyruvate, furnished 6 : 7-dimethoxy-1 : 2 : 3 : 4-tetrahydrocarbazole and ethyl 5 : 6-dimethoxyindole-2-carboxylate, respectively. Both these substances gave the "brucine reaction" with nitric acid, thus affording some support for the view that in brucine the two methoxyl groups are in the ortho-position.[18]

Isatin.—There has been considerable activity in the preparation and study of derivatives of isatin, some of which have found application in medicine. Although these new substances are important in many ways, they are not of sufficient general interest to warrant detailed attention here.

About 1840, Laurent and Erdmann independently studied the action of ammonia on isatin under various conditions and isolated a number of compounds to which several investigators have recently devoted attention. A. Reissert and H. Hoppmann [19] find that Laurent's "isatinammonia" is 3-amino-3-hydroxy-2-ketodihydroindole (I) and is the primary product of the reaction. Isatin-3-imide (II) (Laurent's "imesatin") is formed when ammonia is passed into the suspension until the isatin is just all dissolved, whilst the prolonged action of ammonia on isatin, suspended in alcohol, produces Laurent's "imasatic or isamic" acid (III), which is 3-isatinimidyl-*o*-aminomandelic acid. If alcohol is replaced by water as the suspending medium, the same substance is formed along with Laurent's "imasatin," which is regarded as 3-isatinimidyl-3-dioxindole (IV), since it can be synthesised by warming isatin with isatinimine in alcohol. "Amasatin" or "isamide" is similarly shown to be 3-isatinimidyl-*o*-aminomandelamide (V).

(I.) $NH<^{C_6H_4}_{CO}>C(OH)\cdot NH_2$ $\qquad$ $NH<^{C_6H_4}_{CO}>C{:}NH$ (II.)

$$NH<^{C_6H_4}_{CO}>C{:}N\cdot C(OH)(CO_2H)\cdot C_6H_4\cdot NH_2 \quad \text{(III.)}$$

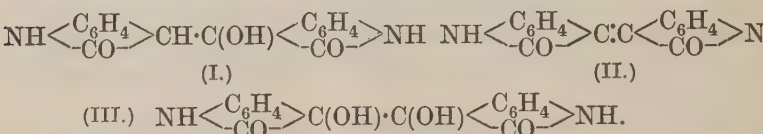
$$NH<^{C_6H_4}_{CO}>C{:}N\cdot C(OH)<^{C_6H_4}_{CO}>NH \quad \text{(IV.)}$$

$$NH<^{C_6H_4}_{CO}>C{:}N\cdot C(OH)(CO\cdot NH_2)\cdot C_6H_4\cdot NH_2 \quad \text{(V.)}$$

It has also been shown [20] that Laurent's "isatan" (Erdmann's "isatide"), obtained by reducing disulphoisatide with ammonium

[18] Compare *J.*, 1925, **127**, 1161. [19] *Ber.*, 1924, **57**, 972; *A.*, 1924, i, 874.
[20] A. Wahl and W. Hansen, *Compt. rend.*, 1924, **178**, 214, 393; *A.*, 1924, i, 322.

hydrogen sulphite, is represented by Lefèvre's formula [21] (I) and yields, when boiled in naphthalene solution, indine which has been shown by various workers [22] to be identical with *iso*indigotin (II). Laurent's "isatide" has been obtained by several investigators by the reduction of isatin and is represented by Lefèvre's formula [22] (III); it is not converted into indine by boiling naphthalene.

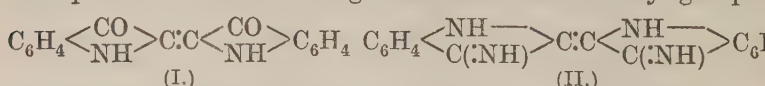


(I.) (II.)

(III.) $NH<_{CO}^{C_6H_4}>C(OH)\cdot C(OH)<_{CO}^{C_6H_4}>NH.$

Disulphoisatide is the sulphur analogue of this, with the ·OH groups replaced by ·SH groups. L. Sander [22] suggests that Laurent's "sulphisatide," produced by the action of hydrogen sulphide on a cold alcoholic solution of isatin, is 3-thioloxindole and states that it is converted by cold alcoholic sodium hydroxide into indine (*iso*indigotin), which in turn is transformed by warm alcoholic soda into Laurent's "hydrindine." The latter is identified as hydroxydihydro*iso*indigotin, to which formula (I) was assigned by P. Friedländer and L. Sander.[23] It therefore appears that "isatan" and "hydrindene" may be identical. It should be added that the *N*-amino-derivative of the substance represented by (I) has been prepared by P. W. Neber and H. Keppler [24] by condensing *l*-aminooxindole with isatin in alcohol.

Indigotin.—Some discussion has taken place regarding the various modifications of the Baeyer formula for indigotin (I) that have from time to time been put forward. W. Madelung and O. Wilhelmi [25] have pointed out that although the imino- and carbonyl groups of



(I.) (II.)

indigotin are not readily responsive to the usual reagents, the presence of the carbonyl groups can be made manifest by the use of such reagents in the case of di-iminoindigotin [26] (II) and from the

[21] L. Lefèvre, *Bull. Soc. chim.*, 1916, [iv], **19**, 113; *A.*, 1916, i, 430. For similar compounds of 7-methylisatin, see A. Wahl and T. Faivret, *Compt. rend.*, 1925, **180**, 589, 790; *A.*, 1925, i, 588; **A.**, 1926, 79; *Ann. Chim.*, 1926, [x], **5**, 314; **A.**, 960.

[22] L. Lefèvre, *Bull. Soc. chim.*, 1916, [iv], **19**, 111; *A.*, 1916, i, 430; compare L. Sander, *Ber.*, 1925, **58**, 820; *A.*, 1925, i, 977.

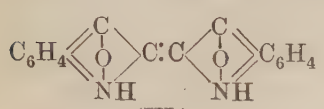
[23] *Ber.*, 1924, **57**, 648; *A.*, 1924, i, 662.

[24] *Ibid.*, p. 778; *A.*, 1924, i, 761.

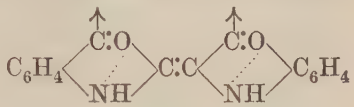
[25] *Ibid.*, p. 234; *A.*, 1924, i, 422; compare, however, Thiele and Pickard, *ibid.*, 1898, **31**, 1252; *A.*, 1898, i, 493.

[26] W. Madelung, *ibid.*, 1913, **46**, 2259; *A.*, 1913, i, 903.

latter it is possible to prepare indigotindioxime [27] and other similar derivatives by the use of the usual reagents. The stability of indigotin also suggests some sort of connexion between the carbonyl and the imino-groups and lends support to such formulæ as those proposed by M. Claasz [28] (III) and by I. Lifschitz and H. Lourié [29]



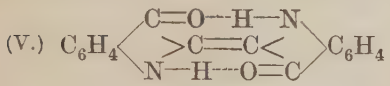
(III.)

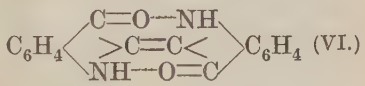


(IV.)

(IV), which only differ on the point of representing the connexion in question by rigid bonds or by residual affinities. Such formulæ are not readily applicable to the dioxime, bisphenylhydrazone, etc., of indigotin, although these derivatives are closely related optically to indigotin itself. Madelung and Wilhelmi therefore prefer a formula of the type developed by Scholl [30] (V) or the modified form

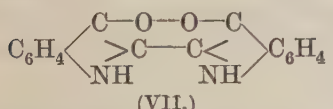
(V.)



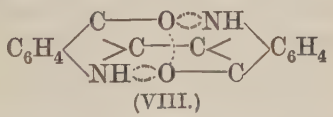


(VI.)

(VI), which has the advantage that it is also applicable to thioindigo and oxindigo, where the :NH group is replaced by the single atoms S and O so that the co-ordinating hydrogen atom shown in (V) is not available. Formulæ (V) and (VI) have the further advantage that they account for the absence of *cis-* and *trans-*isomerism in indigotin, which is required by the Baeyer formula, although some workers have specified a preference for either the *cis-* [31a] or *trans-* [31b] form as representing ordinary indigotin, at least in some of its reactions. On this particular point, R. Robinson [32] has put forward the formula (VII) or its extension (VIII), which also



(VII.)



(VIII.)

satisfactorily accounts for the absence of a second form. A new formula in detailed (IX*a*) and simplified (IX*b*) forms has also been

[27] *Annalen*, 1914, **405**, 58; *A.*, 1914, i, 738.

[28] *Ber.*, 1916, **49**, 2079; *A.*, 1916, i, 839.

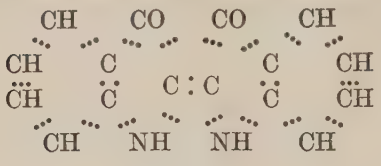
[29] *Ibid.*, 1917, **50**, 897; *A.*, 1917, i, 586.

[30] Georgievic's "Die Beziehungen zwischen Farbe und Konstitution von Farbstoffen," 1920. Compare T. M. Lowry, *J. Soc. Chem. Ind.*, 1925, **44**, 230.

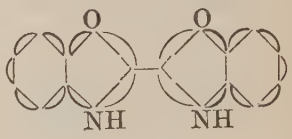
[31] See, for example, (*a*) K. G. Falk and J. M. Nelson, *J. Amer. Chem. Soc.*, 1907, **29**, 1739; *A.*, 1908, i, 107; (*b*) T. Posner and W. Kemper, *Ber.*, 1924, **57**, 1311; *A.*, 1924, i, 1237.

[32] *J. Soc. Dyers Col.*, 1921, **37**, 77.

suggested by H. King [33] based on the J. J. Thomson formula for benzene, which accounts at least as well as anything yet suggested for the various anomalies referred to above.



(IX*a*.)

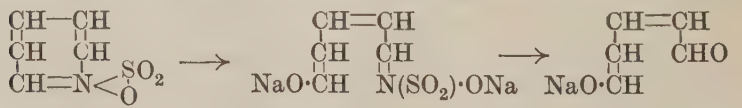


(IX*b*.)

Pyridine Derivatives.

A comparatively simple method of obtaining pure pyridine has been described, depending upon the preparation of the perchlorate, which is much less soluble than those of the bases usually accompanying pyridine in the commercial product.[34]

A fuller account has now been given of the degradation of pyridine to glutacondialdehyde.[35] Pyridinium-1-sulphonic acid (I), obtained by the action of various sulphonating agents on pyridine in carbon tetrachloride, on treatment with cold concentrated sodium hydroxide solution, yields the disodium derivative of α-imino-ε-hydroxy-$\Delta^{\beta\delta}$-pentadiene-*N*-sulphonic acid (II), which is hydrolysed by warm alkalis to the sodium derivative of enolic glutacondialdehyde (III).



(I.) (II.) (III.)

The inverse process of building up pyridine and its derivatives has also received some attention. L. E. Hinkel and W. R. Madel have observed that the substitution of a bromine atom or a nitro-group in position 3 in *p*-dimethylaminobenzaldehyde leads to an increased yield of the dimethyldihydropyridine derivative obtained in Hantzsch's condensation process.[36]

Carbazide (or azoimide) dissolved in benzene and heated to 150° in a closed vessel produces pyridine and if the pressure be maintained at 6 to 7 atmospheres during the process some aniline also is formed. With toluene the products are γ-picoline and toluidine and with *p*-cymene, carvacrylamine and 2-methyl-5-*iso*propylpyridine.[37]

[33] *J. Soc. Chem. Ind.*, 1925, **44**, 135, 285; compare Lowry, *loc. cit.*

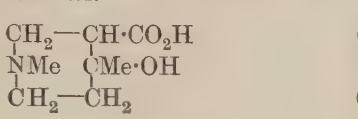
[34] F. Arndt, A. Kirsch, and P. Nachtwey, *Ber.*, 1926, **59**, 1074; **A.**, 843.

[35] P. Baumgarten, *ibid.*, 1926, **59**, 1166; **A.**, 844; compare *Ann. Reports*, 1924, **21**, 125.

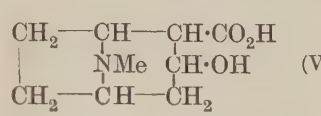
[36] *J.*, 1926, 161; **A.**, 413.

[37] T. Curtius and A. Bertho, *Sitzungsber. Heidelberg. Akad. Wiss., A.*, 1924, 3; 1925, 3; **A.**, 1926, 1152.

When a solution of acetone, formaldehyde, and methylamine hydrochloride is boiled for 8 hours, racemic α- and β-forms of 4-hydroxy-3-acetyl-1 : 4-dimethylpiperidine are produced.[38] On oxidation with barium hypobromite, both are converted into the 3-carboxylic acids (IV), which are of interest owing to their partial similarity to ecgonine (V) in structure and to the fact that, like the latter base, they yield local anæsthetics on benzoylation, followed by esterification with methyl alcohol.



(IV.)



(V.)

It has been assumed hitherto that the condensation of *iso*valeraldehyde with ammonia in presence of alumina gave as sole product 3 : 5-di*iso*propyl-2-*iso*butylpyridine, but it now appears [39] that two other bases are also formed, (*a*) 3 : 5-di*iso*propyl-4-*iso*butylpyridine and (*b*) 3 : 5-di*iso*propylpyridine. A series of alkylpyridines has also been made by the action of organo-magnesium halides on α-piperidino-nitriles, the cyanogen group of the latter being replaced by the alkyl radical of the magnesium compound.[40]

Contrary to the experience of H. Meyer [41] that 2- and 4-pyridones do not acylate, A. E. Tschitschibabin and co-workers have been able to prepare benzoyl and *p*-nitrobenzoyl derivatives of 2-pyridone, and also an acetyl derivative, which, however, is only formed in the absence of water.[42] Among other investigations on derivatives of pyridine, reference may be made to a number of papers on 2-, 4-, and 2 : 5-aminopyridines [43] and on hydrazo- and azo-derivatives of pyridine,[44] which contain much useful information but cannot be dealt with here in the necessary detail to be of value. Nitration experiments with 2-, 3-, and 4-phenylpyridines show that the pyridinium residue has mainly a para-directive effect, although in the case of 2- and 4-phenylpyridines a considerable amount of *m*-nitr-

[38] C. Mannich, with G. Ball and L. Stein, *Arch. Pharm.*, 1926, **264**, 65, 77; **A.**, 522, 523.

[39] (Mlle.) M. P. Oparina, *J. Russ. Phys. Chem. Soc.*, 1925, **57**, 319; **A.**, 1926, 844; compare H. Ljubavin, *A.*, 1873, 1023; A. E. Tschitschibabin and co-workers, *A.*, 1906, i, 451; 1923, i, 1121, 1122, 1123.

[40] M. Velghe, *Bull. Soc. chim. Belg.*, 1926, **35**, 229; **A.**, 1044.

[41] *Monatsh.*, 1905, **26**, 1303; *A.*, 1906, i, 107.

[42] *J. Russ. Phys. Chem. Soc.*, 1925, **56**, 153; **A.**, 1926, 179; *Ber.*, 1925, **58**, 2650; **A.**, 1926, 179.

[43] A. E. Tschitschibabin and others, *Ber.*, 1926, **59**, 2048, 2055; **A.**, 1153; *J. Russ. Phys. Chem. Soc.*, 1926, **57**, 297, 301; **A.**, 845; L. Schmid and B. Becker, *Monatsh.*, 1926, **46**, 671, 675; **A.**, 845.

[44] E. Königs and others, *Ber.*, 1925, **58**, 2571; 1926, **59**, 316, 321; **A.**,178 412, 413.

ation occurs.[45] The carboxyl groups in potassium collidine-3 : 5-dicarboxylate are not replaced by nitro-groups on heating with nitric acid up to 200°. Nitration of collidine itself with nitric and fuming sulphuric acids produces 3-nitro-2 : 4 : 6-trimethylpyridine.[46]

Quinoline Group.

J. Meisenheimer and E. Stotz,[47] after a critical survey of the literature of the dihydroquinolines, conclude that the substances prepared by M. Freund and E. Speyer [48] by the action of organo-magnesium halides on quinoline methiodides are, as then suggested, 1-methyl-2-alkyl-1 : 2-dihydroquinolines, showing but little tendency to polymerise, except in the case of the 2-phenyl derivative. A second group made by G. Heller and co-workers,[49] by reduction with zinc dust of the pseudo-bases precipitated from solutions of quinoline methiodides by sodium hydroxide, are bimolecular and were assigned formula (II), mainly on the ground that identical products were obtained by the reduction of Freund's bases (I), the nascent hydrogen being assumed to catalyse polymerisation. It is suggested as more likely that Heller's process produces first unstable 1 : 4-dihydro-compounds, which then polymerise, with the formation of a new tetramethylene ring (III).

(I.) (II.) (III.)

The third group described by Räth,[50] as produced by the action of halogenoacetals on toluidines, is not, as assumed by that author, identical with Freund's bases and, according to W. König and R. Buchheim,[51] the chief product of the action of chloro- or bromo-acetal on *o*-toluidine is 4-ethyl-*o*-toluidine. In this connexion, it is interesting to note that F. A. Mason [52] has found, on re-examination of his product, that it is 2-methylquinoline and not 1 : 2-dihydroquinaldine. Similarly, the "4-keto-2-methyl-1 : 4-dihydro-

[45] R. Forsyth and F. L. Pyman, *J.*, 1926, 2912; compare *this Report*, p. 175.

[46] P. J. van Rijn, *Rec. trav. chim.*, 1926, **45**, 267; **A.**, 525.

[47] *Ber.*, 1925, **58**, 2330; with K. Bauer, 2320; **A.**, 1926, 76.

[48] *Ibid.*, 1904, **37**, 4666; *A.*, 1905, i, 156.

[49] *Ibid.*, 1914, **47**, 2893; *A.*, 1915, i, 300; compare W. H. Mills and R. Raper, *J.*, 1925, **127**, 2466; **A.**, 1926, 77; E. Rosenhauer, H. Hoffmann, A. Schmidt, and H. Unger, *Ber.*, 1926, **59**, 946, 2356; **A.**, 735, 1260; and *Ann. Reports*, 1923, **20**, 151; 1925, **22**, 143.

[50] *Ber.*, 1924, **57**, 550, 715; *A.*, 1924, i, 555, 667.

[51] *Ibid.*, 1925, **58**, 2868; **A.**, 1926, 178.

[52] *J.*, 1926, 955; compare *J.*, 1925, **127**, 1032.

quinoline " obtained by G. Heller and A. Sourlis [53] by the reduction of *o*-nitrophenylhydroxyethyl methyl ketone with zinc dust and cold 33% acetic acid is, according to J. Meisenheimer and E. Stotz, 2-methylquinoline *N*-oxide, and similar *N*-oxides have been prepared from pyridine and *iso*quinoline.[54]

E. Rosenhauer and H. Hoffmann [49] have prepared three more examples of the crystalline 2-methylenedihydroquinoline bases referred to last year. These were obtained by the cautious addition of dilute sodium hydroxide solution to aqueous solutions of 2-methyl-, 2 : 4-dimethyl-, and 2 : 4 : 6-trimethyl-quinoline methosulphate (methiodide in the latter two cases), followed by immediate extraction with ether. This process is practically identical with Heller's method of obtaining " methyldihydroquinolines " and probably explains some of the anomalies referred to in the discussion by Meisenheimer and Stotz referred to above. J. E. Humphries also has found that the interaction of 2-methylquinoline and allied bases or their quaternary salts with 4 : 4′-tetramethyldiaminobenzhydrol in presence of acetic acid affords another instance of the anomalous reactivity of the 2-methyl group in heterocyclic compounds.[55]

4-Methoxy-2-methylquinoline condenses under ordinary conditions with aromatic aldehydes to produce the corresponding 4-methoxy-2-styrylquinolines, but if the reaction takes place under pressure, wandering of the methyl group occurs and some of the corresponding 2-styryl-1-methyl-4-quinolone is also formed. Piperonal is exceptional in giving only one product, the alkaloid dehydrocusparine.[56] A normal condensation also takes place between *m*-nitrobenzaldehyde and 2-methylquinoline, the sole product being 2-*m*-nitrostyrylquinoline.[57]

A series of amino-derivatives of styryl- and anil-quinolines has been prepared for bactericidal examination. Of the two series, the styryl derivatives are the more powerful antiseptics and as a rule the potency is increased by methylation or acylation of the amino-group, sulphonation or other methods of increasing the solubility, or the introduction of a further condensed nucleus. The styryl side-chain is less effective in position 4 than in position 2, and acidic groups in position 6 lower the activity, which is completely lost with an azo-group in this position.[58]

[53] *Ber.*, 1908, **41**, 2692; *A.*, 1908, i, 913.

[54] *Ibid.*, 1925, **58**, 2334; 1926, **59**, 1848; **A.**, 77, 1152.

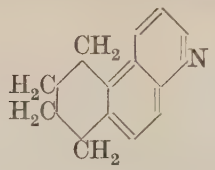
[55] *J.*, 1926, 374; **A.**, 414.

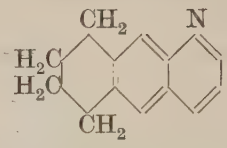
[56] J. Tröger and E. Dunker, *J. pr. Chem.*, 1926, [ii], **112**, 196; **A.**, 525; compare *Ann. Reports*, 1924, **21**, 131; 1925, **22**, 142.

[57] T. W. J. Taylor and C. P. Woodhouse, *J.*, 1926, 2971; compare W. Wartanian, *Ber.*, 1890, **23**, 3645; *A.*, 1891, i, 329.

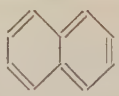
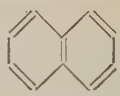
[58] C. H. Browning, J. B. Cohen, S. Ellingworth, and R. Gulbransen, *Proc. Roy. Soc.*, 1926, [*B*], **100**, 293; **A.**, 1153.

Naphthaquinolines of two types, angular (I) and linear (II), are known to be produced simultaneously by the application of the Skraup reaction to *ar*-tetrahydro-β-naphthylamine.[59]

(I.) 

 (II.)

Both types are also formed in the quinaldine synthesis with either *ar*-tetrahydro-α- or -β-naphthylamine [60] and the course of the reaction has been investigated in the latter case. A nearly quantitative separation of the two β-isomerides can be effected through the hydriodides, that of the *ang.*-isomeride being almost insoluble when precipitated in dilute hydrochloric acid. The total yield of the crude mixed bases is 35% of the theoretical, of which 65% is the angular isomeride (3-methyl-7 : 8 : 9 : 10-tetrahydro-β-naphthaquinoline, Type I), the remainder being the linear base (2-methyl-6 : 7 : 8 : 9-tetrahydro-α-anthrapyridine, Type II). From these data, it is concluded that the tetramethylene group in *ar*-tetrahydro-β-naphthylamine, used as a primary material in the quinaldine synthesis, has no directive influence in the formation of the third ring and that the energy content determines which isomeride will be formed. The energy content of the four systems is in the order

(III.) (IV.) (V.)   (VI.)

(III)>(IV) and (VI)>(V). Systems (III) and (V) should yield linear, and systems (IV) and (VI) angular tricyclic compounds. The energy difference between (V) and (VI) is so marked that β-naphthylamine gives angular compounds exclusively. The difference between (III) and (IV) is less marked, hence a mixture of isomerides is formed with the angular form predominant in the case of *ar*-tetrahydro-β-naphthylamine.

A number of naphthaquinoline and naphtha*iso*quinoline derivatives have been prepared by C. S. Gibson, K. V. Hariharan, K. N. Menon, and J. L. Simonsen.[61] The condensation of β-naphthylamine with paraldehyde [62] was found to proceed smoothly (to *dl*-1-methyl-1 : 2 : 3 : 4-tetrahydro-β-naphthaquinoline as a final pro-

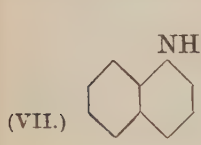
[59] J. von Braun and H. Gruber, *Ber.*, 1922, **55**, 1710; *A.*, 1922, i, 762.

[60] J. Lindner and others, *Monatsh.*, 1924, **44**, 337; 1925, **46**, 225, 231; *A.*, 1924, i, 1102; **A.**, 1926, 410.

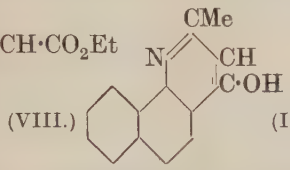
[61] *J.*, 1926, 2247; **A.**, 1154.

[62] O. Doebner and W. von Miller, *Ber.*, 1884, **17**, 1711; *A.*, 1884, 1373.

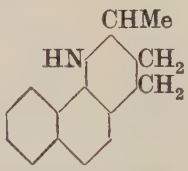
duct, through 3-chloro-1-methyl-β-naphthaquinoline as described below), but 2-methyl-α-naphthaquinoline could not be obtained by condensing α-naphthylamine with paraldehyde as described by Doebner and von Miller and recourse was had to a modification of Knorr's method,[63] *viz.*, condensation of α-naphthylamine with ethyl acetoacetate, the new feature being the use of diethylamine as a catalyst. By this means, ethyl β-1-naphthylaminocrotonate (VII) was obtained, which on heating at 240° was converted into 4-hydroxy-2-methyl-α-naphthaquinoline (VIII), and this yielded *dl*-2-methyl-1 : 2 : 3 : 4-tetrahydro-α-naphthaquinoline (IX) by treatment with phosphorus pentachloride followed by reduction of the 4-chloro-derivative with sodium and ethyl alcohol.



(VII.)



(VIII.)

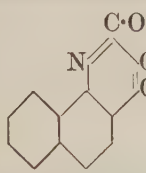


(IX.)

Under the conditions prescribed by Knorr,[63] the main product is *s*-di-α-naphthylcarbamide,[64] accompanied by some β-1-naphthylaminocrotono-α-naphthylamide (X); the latter can be hydrolysed to acetoaceto-α-naphthalide (XI), which can with difficulty be induced to undergo ring closure to 2-hydroxy-4-methyl-α-naphthaquinoline (XII). From this, the corresponding tetrahydro-derivative can be made through the chloro-compound as described above.

(X.) $C_{10}H_7 \cdot NH \cdot CO \cdot CH{:}CMe \cdot NH \cdot C_{10}H_7$

(XI.) $C_{10}H_7 \cdot NH \cdot CO \cdot CH_2 \cdot COMe$



(XII.)

These difficulties in the use of α-naphthylamine as a primary material in the synthesis of naphthaquinolines are not encountered in the case of the 4-nitro- and 4-bromo-α-naphthylamines, which readily condense with paraldehyde, furnishing the corresponding 6-nitro- or 6-bromo-2-methyl-α-naphthaquinoline. The importance of substituents in position 4 in facilitating condensation with paraldehyde is emphasised by S. U. Nair and J. L. Simonsen in a later paper describing the preparation of a series of acenaphthpyridines.[65]

Comparatively little work has been done during the year on naturally-occurring quinoline bases. It has been shown that the

[63] L. Knorr, *Ber.*, 1884, **17**, 543; *A.*, 1884, 1198; compare M. Conrad and L. Limpach, *ibid.*, 1888, **20**, 531; *A.*, 1888, 503.

[64] Compare (Miss) W. G. Hurst and J. F. Thorpe, *J.*, 1915, **107**, 934.

[65] *J.*, 1926, 3140.

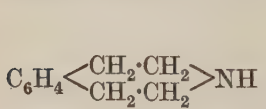
β-acid formed by the hydrolysis of oryzanin from rice is 2 : 6-dihydroxyquinoline-4-carboxylic acid.[66] No success attended attempts to introduce arsinic acid residues into diazotised solutions of various amino-derivatives of reduced cinchona alkaloids,[67] but arsino-derivatives of phenylcinchoninic acid can be so made [68] and are capable of reduction to arseno-compounds. By the use of arsenic trichloride on dehydroquinine, the arsenical compound (I; Q = the quinolyl and Q′ = the quinuclidine nucleus) [69] is produced. On treatment with ammonium carbonate solution, one of the arsenic groups is lost with the formation of chloroarsinosoquinine (II). With quinine and dihydroquinine the compounds $C_{20}H_{25}O_2N_2Cl_4As$

$$\underset{\text{(I.)}}{AsCl_2\cdot CH{:}CCl\cdot Q'(HCl)\cdot CH(O\cdot AsCl_2)\cdot Q(OMe),HCl} \xrightarrow[\text{ammonium carbonate)}]{\text{(by action of}} \underset{\text{(II.)}}{AsO\cdot CH{:}CCl\cdot Q'\cdot CH(OH)\cdot Q\cdot OMe}$$

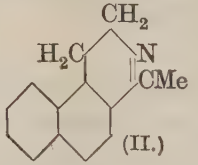
and $C_{20}H_{27}O_2N_2Cl_4As$ are formed; these are converted by ammonium carbonate solution into the arsenious esters, $C_{20}H_{23}O_3N_2As$ and $C_{20}H_{25}O_3N_2As$, which contain the arsenic atom united to the secondary alcohol group thus, –CH·O·AsO.

iso*Quinoline Group.*

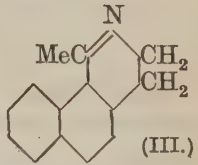
What is regarded as the *trans*-form of decahydro*iso*quinoline has been prepared by L. Helfer [70] from *trans-o*-carboxy*cyclo*hexane-acetic acid [71] by converting the latter into its imide and reducing this with sodium and boiling amyl alcohol. Reduction of the lactam of *o*-β-aminoethylphenylacetic acid by sodium and ethyl alcohol produces a mixture of bases from which *s*-homotetrahydro-*iso*quinoline (I) was isolated with *o*-β′-aminoethyl-β-phenylethyl alcohol, $NH_2\cdot CH_2\cdot CH_2\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot OH$, as a by-product.[72]



(I.)



(II.)



(III.)

[66] Y. Sahashi, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1926, **4**, 207; **A.**, 846.

[67] F. X. Erben, E. Philippi, and O. Maulwurf, *Ber.*, 1926, **59**, 2150; **A.**, 1159.

[68] H. O. Calvery, C. R. Noller, and R. Adams, *J. Amer. Chem. Soc.*, 1925, **47**, 3058; **A.**, 1926, 187.

[69] F. X. Erben and others, *Ber.*, 1925, **58**, 2854; **A.**, 1926, 188.

[70] *Helv. Chim. Acta*, 1926, **9**, 814; **A.**, 1150. For *cis*-form, see *ibid.*, 1923, **6**, 785; *A.*, 1923, i, 1228.

[71] A. Windaus, W. Hückel, and G. Reverey, *Ber.*, 1923, **56**, 91; *A.*, 1923, i, 220.

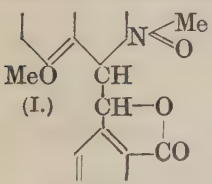
[72] J. von Braun and H. Reich, *Annalen*, 1925, **445**, 225; *A.*, 1925, i, 1405; *Ber.*, 1925, **58**, 2765; **A.**, 1926, 178.

It has been found feasible to prepare naphtha*iso*quinolines [61] by the application of a method [73] used by Kaufmann and Radosević for the preparation of simple *iso*quinolines, which depends on treatment of the oximes of γ-ketobutylbenzenes with phosphorus pentachloride. α- and β-Naphthaldehydes condense readily with acetone to give 1- and 2-γ-ketobutenylnaphthalenes, $C_{10}H_7 \cdot CH{:}CH \cdot COMe$, which on catalytic reduction furnish γ-ketobutylnaphthalenes, $C_{10}H_7 \cdot CH_2 \cdot CH_2 \cdot COMe$; from the oximes of these, 4-methyl-1 : 2-dihydro-β-naphtha*iso*quinoline (II) and 1-methyl-3 : 4-dihydro-α-naphtha*iso*quinoline (III), respectively, were obtained although in small yield.

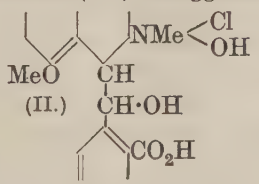
This year's work includes many important papers on alkaloids of this group. These alkaloids belong to three types : (A) benzyl-*iso*quinolines with a sub-section of meconyl*iso*quinolines; (B) di-*iso*quinolines, including alkaloids such as cryptopine, developed from it; and (C) the phenanthreno*iso*quinolines with morphine and the related alkaloids, codeine and thebaine, as a sub-section. Means of converting type (A) into type (B) or (C) are now well known.

*Benzyliso**quinolines*.—A considerable number of these products have been prepared in preliminary attempts to synthesise (1) members of the di*iso*quinoline or berberine group of alkaloids,[74] to which reference has been made in the last two Reports of this series, and (2) representatives of the phenanthrene group of *iso*quinoline alkaloids to which attention is directed later in this Report.[75]

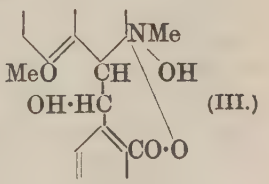
The formation of *N*-oxides when heterocyclic bases and alkaloids are treated with hydrogen peroxide, perbenzoic acid, and similar oxidising agents is now well known. A. M. Drummond and A. McMillan [76] have prepared a derivative of this type (I) from narcotine, the reactions of which indicate that it is a true *N*-oxide in which the structure of narcotine is preserved. It yields a crystalline hydrochloride which contains a free carboxyl group, and is therefore represented by (II), and is readily hydrolysed to a hydroxy-acid, from which the hydrochloride can be regenerated, and for which the betaine structure (III) is suggested.



(I.)



(II.)



(III.)

[73] *Ber.*, 1916, **49**, 675; *A.*, 1916, i, 502.

[74] R. D. Haworth and W. H. Perkin, jun., *J.*, 1925, **127**, 1434; *A.*, 1925, i, 968; R. D. Haworth, W.H. Perkin, jun., and J. Rankin, *ibid.*, p. 1444; *A.*, 1925, i, 969; *Ann. Reports*, 1924, **21**, 133; 1925, **22**, 145.

[75] R. Robinson and (Miss) H. West, *J.*, 1926, 1985; **A.**, 1045.

[76] *J.*, 1926, 2702; **A.**, 1263.

Mention was made last year [77] of the proof by E. Späth and co-workers that the alkaloid tritopine is merely impure laudanidine and that, since the latter is converted into *l*-laudanosine by diazomethane, whilst laudanine on similar treatment yields *dl*-laudanosine, and both on ethylation and oxidation of the ethyl ether furnish 4-methoxy-3-ethoxybenzoic acid,[78] laudanidine must be the lævo-form of laudanine. This year the same investigators, continuing this work on the minor alkaloids of opium, have shown that pseudopapaverine, to which O. Hesse assigned the formula $C_{21}H_{21}O_4N$, is merely impure papaverine, $C_{20}H_{21}O_4N$, and that König's methylenepapaverine, $C_{21}H_{21}O_4N$, obtained by the condensation of papaverine with formaldehyde, yields papaveraldine on oxidation, takes up two atoms of hydrogen to form a dihydro-derivative, and therefore must have the constitution shown below.[79] Similarly, they have found that codamine, $C_{17}H_{15}(OH)(OMe)_3N$, on methylation furnishes *d*-laudanosine, but on ethylation and oxidation of the ethyl ether, 3 : 4-dimethoxybenzoic (veratric) acid was obtained, so that in this case the free hydroxyl group of codamine, represented by the ethoxy-group in the ethyl ether oxidised, must be in the quinoline and not in the benzyl nucleus. Codamine therefore is not *d*-laudanidine. The second product of the oxidation proved to be the mixed methyl and ethyl ether of nor-*m*-hemipinic acid, which leaves it certain that the free hydroxyl group of codamine occupies either position 6 or 7 in the *iso*quinoline nucleus. The decision in favour of position 7 was reached by (1) discovering the conditions under which *dl*-laudanosine could be oxidised to *N*-methylcorydaldine, a substance which has been synthesised and about whose constitution there is no doubt, (2) synthesising the two mixed ethers (ethoxy in 6 or 7, methoxy in 7 or 6) corresponding to *N*-methylcorydaldine, and (3) oxidising the ethyl ether of codamine (a homolaudanosine) under the conditions determined in (1) and identifying the "corydaldine" produced with one of the mixed ethers referred to under (2). The product in question proved to be 6-methoxy-7-ethoxy-*N*-methylcorydaldine [80] (I below).

In early attempts to synthesise laudanine, H. Decker and T. Eichler [81] obtained an isomeride, pseudolaudanine, which they regarded as a laudanosine in which one of the four methoxyl groups, and probably one in the *iso*quinoline nucleus, is replaced by hydroxyl. This speculation brings pseudolaudanine into close relationship

[77] *Ann. Reports*, 1925, **22**, 152.

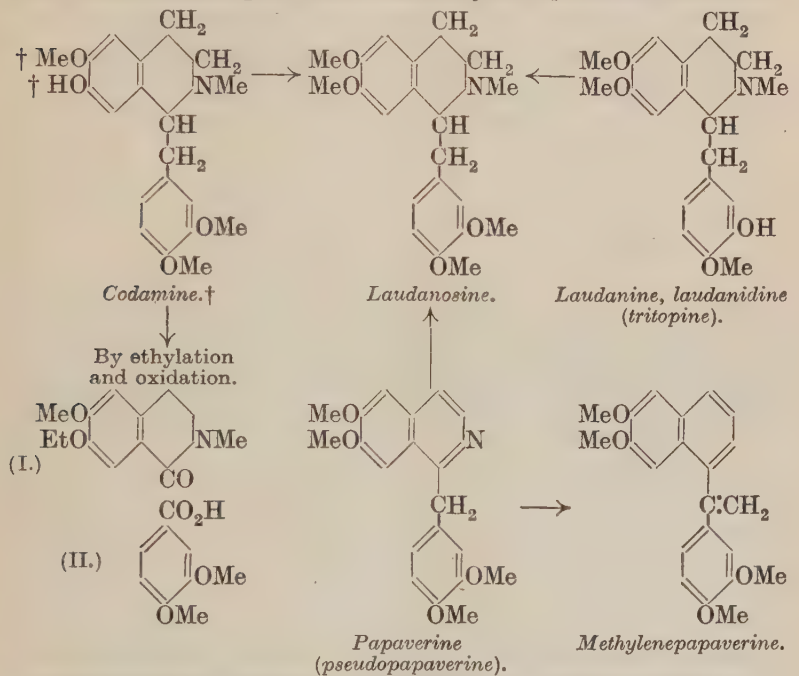
[78] E. Späth [with R. Seka], *Ber.*, 1925, **58**, 1272; *A.*, 1925, i, 1093; [with E. Bernhauer], *ibid.*, p. 200; *A.*, 1925, i, 294.

[79] E. Späth and N. Polgar, *Ber.*, 1926, **59**, 2787.

[80] E. Späth and H. Epstein, *ibid.*, p. 2791.

[81] *Annalen*, 1913, **395**, 377; *A.*, 1913, i, 289.

with codamine, since it would be either *dl*-codamine, or the latter with the positions of the hydroxyl and methoxyl groups in the *iso*-quinoline nucleus interchanged. The latter is now found to state the relationship correctly since, by the process outlined above, it yields on oxidation 7-methoxy-6-ethoxy-*N*-methylcorydaldine (compare I below). The foregoing proofs rest on the correct formulation of laudanosine and laudanine, both of which have been synthesised by methods which leave no doubt of their constitution.[82] The inter-relationships of these bases may be represented as follows :



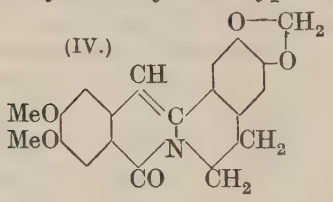
† Codamine with –OMe and –OH interchanged = pseudolaudanine.

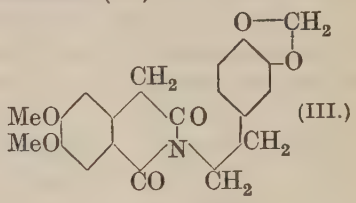
Diisoquinoline Alkaloids.—The transition from the benzyl*iso*-quinolines to the di*iso*quinolines is effected by the insertion of a CH_2 group between positions 2 and 2′ (berberine series) or 2 and 6′ (pseudoberberine series), the latter being the position usually taken up in the direct synthesis of such products, and in attempts to synthesise the natural alkaloids of this type it has been necessary to build up the heterocyclic ring of *iso*quinoline as in the synthesis of oxyberberine effected recently.[83] On the same lines, substances

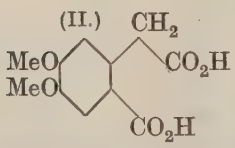
[82] A. Pictet and (Mlle.) M. Finkelstein, *Compt. rend.*, 1909, **148**, 925; *A.*, 1909, i, 323; E. Späth and N. Lang, *Monatsh.*, 1921, **42**, 273; *A.*, 1922, i, 568.

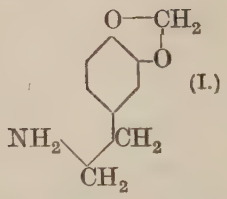
[83] Compare *Ann. Reports*, 1924, **21**, 133; 1925, **22**, 146.

allied to oxyberberine have been obtained [84] by condensing homopiperonylamine (I) with homophthalic acid and with 4 : 5-dimethoxyphthalic acid (II), producing in the latter case 2-homopiperonyl-6 : 7-dimethoxyhomophthalimide (III), which is converted by alkalis into the corresponding amic acid, the methyl ester of which on dehydration yields oxypseudoberberine (IV).

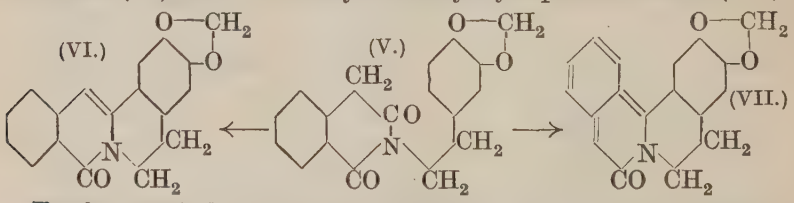








The condensation with homophthalic acid gives rise in like manner to 2-homopiperonylhomophthalimide (V), but in this case the methyl ester of the corresponding amic acid, on treatment with phosphorus oxychloride, yields two products, 2 : 3-methylenedioxyoxyprotoberberine (VI) and 2 : 3-methylenedioxyoxy*iso*protoberberine (VII).



Further work has also been done on the Corydalis alkaloids. The method described last year [85] for the conversion of berberine into palmatine and jatrorrhizine has been applied to *d*-, *l*-, and *dl*-tetrahydroberberines and has furnished the corresponding *d*-, *l*-, and *dl*-tetrahydropalmatines.[86] The constitutions assigned to corybulbine and *iso*corybulbine [87] have been confirmed by independent work [88] and by their simultaneous formation by the partial demethylation of corydaline [89] by heating this for a short time with

[84] R. D. Haworth, W. H. Perkin, jun., and H. S. Pink, *J.*, 1925, **127**, 1709; *A.*, 1925, i, 1168.

[85] *Ann. Reports*, 1925, **22**, 151.

[86] E. Späth and E. Mosettig, *Ber.*, 1926, **59**, 1496; **A.**, 965.

[87] *Ann. Reports*, 1925, **22**, 150.

[88] J. Gadamer and K. Sawai, *Arch. Pharm.*, 1926, **264**, 401; **A.**, 1161.

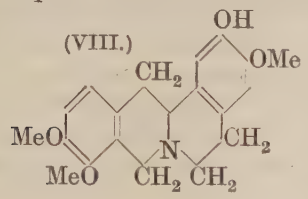
[89] E. Späth and H. Holter, *Ber.*, 1926, **59**, 2800.

hydrochloric acid. From calumba root, E. Späth and G. Burger [90] have isolated a new alkaloid, tetrahydrocolumbamine,

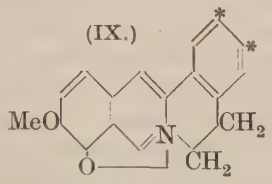
$$C_{17}H_{13}N(OH)(OMe)_3,$$

which is converted by diazomethane into *dl*-tetrahydropalmatine and by diazoethane into a monoethyl ether, which on oxidation yields, like *iso*corybulbine, 6-methoxy-7-ethoxy-1-keto-1 : 2 : 3 : 4-tetrahydro*iso*quinoline and must therefore have the constitution (VIII).

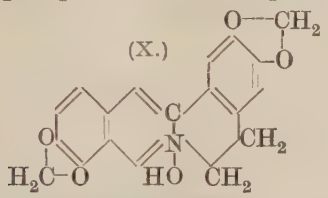
(VIII.)



(IX.)



(X.)



Berberrubine [91] and palmatrubine [92] are produced by heating berberinium and palmatinium chlorides, respectively, and both have been regarded as similarly constituted, since they are reconverted into the iodides or other salts of the parent alkaloids on treatment with methyl esters. It has now been found that tetrahydroberberrubine ethyl ether on oxidation furnishes hydrastic acid and 4-methoxy-3-ethoxyphthalic acid, whilst tetrahydropalmatrubine ethyl ether yields *m*-hemipinic acid and 4-methoxy-3-ethoxyphthalic acid. Berberrubine and palmatrubine are therefore regarded as phenol-betaines (IX) in which the positions marked * are occupied by a dioxymethylene group and two methoxy-groups, respectively.[90]

Coptis japonica has been shown by Z. Kitasato [93] to contain a new alkaloid, coptisine, $C_{19}H_{15}O_5N$. This is regarded as 2 : 3 : 9 : 10-bismethylenedioxyprotoberberine (X),[94] since by the prolonged action of phloroglucinol and sulphuric acid it is converted, by loss of two dioxymethylene groups,[95] into an unstable phenolic base, which on methylation and reduction furnishes tetrahydropalmatine. This alkaloid is closely related to a series of products prepared by R. D. Haworth and W. H. Perkin in the course of their synthesis

[90] *Ber.*, 1926, **59**, 1486; **A.**, 963; and compare *Ann. Reports*, 1925, **22**, 151.

[91] C. Frerichs and P. Stoepel, *Arch. Pharm.*, 1913, **251**, 321; *A.*, 1913, i, 1094; K. Feist and Sandstede, *ibid.*, 1918, **256**, 1.

[92] K. Feist and G. L. Dschu, *ibid.*, 1925, **263**, 294; *A.*, 1925, i, 830.

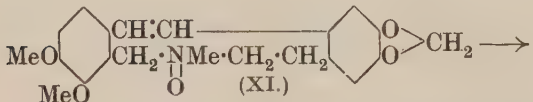
[93] *Proc. Imp. Acad. Tokyo*, 1926, **2**, 124; **A.**, 1160.

[94] For nomenclature, see *Ann. Reports*, 1925, **22**, 145.

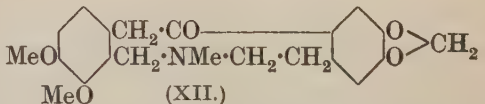
[95] Compare E. Späth and H. Quietensky, *Ber.*, 1925, **58**, 2267; **A.**, 1926, 82.

of protopine (*see below*); thus the tetrahydro-derivative, m. p. 215°, used in the purification of coptisine must be identical with the latter authors' 2 : 3 : 9 : 10-bismethylenedioxytetrahydroprotoberberine, m. p. 219°.[96] Coptisine is also of some biological interest, since all the species of *Coptis* so far examined are stated to have yielded berberine.

Important contributions have been made during the year to the chemistry of the cryptopine section of di*iso*quinoline alkaloids by the conversion of berberine into β-homochelidonine [97] (α-*allo*cryptopine) and by the synthesis of cryptopine and protopine.[98] The former transformation was effected by converting anhydrotetrahydromethylberberine, by treatment with perbenzoic acid in chloroform–ether solution below 5°, into the amine oxide (XI), which in presence of acetic and hydrochloric acids isomerises to α-*allo*cryptopine (XII).

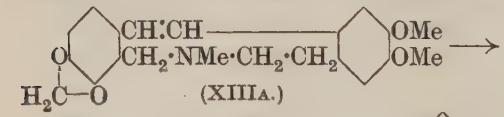


(XI.)

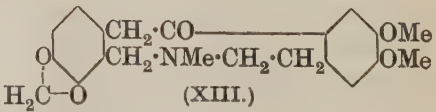


(XII.)

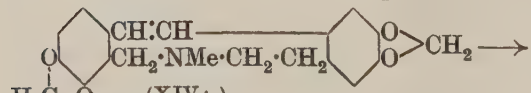
The final stages in the synthesis of cryptopine (XIII) and protopine (XIV) have been achieved by the same method, *viz.*, the oxidation of anhydrodihydrocryptopine-A (XIIIA) and anhydrodihydroprotopine-A (XIVA), respectively, with perbenzoic acid and isomerisation of the resulting amine oxides.[98]



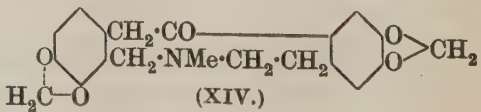
(XIIIA.)



(XIII.)



(XIVA.)



(XIV.)

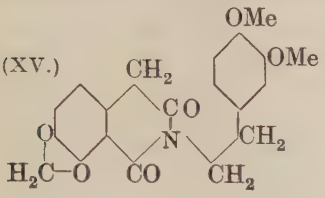
[96] *J.*, 1926, 1780, 1781.

[97] R. D. Haworth and W. H. Perkin, jun., *J.*, 1926, 445; **A.**, 417.

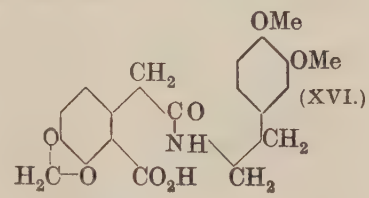
[98] *Idem, ibid.*, p. 1769; **A.**, 964.

The preparation of the initial materials for these final stages involved the discovery of a method for making 3 : 4-methylenedioxyhomophthalic acid.[99] This was then condensed with β-veratrylethylamine to *N*-β-veratrylethyl-3 : 4-methylenedioxyhomophthalimide (XV), and this converted into the corresponding amic acid (XVI), the methyl ester of which was transformed by phosphorus oxychloride [1] into oxy*epi*berberine [2] (XVII).

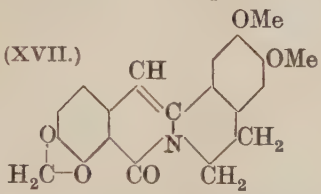
(XV.)



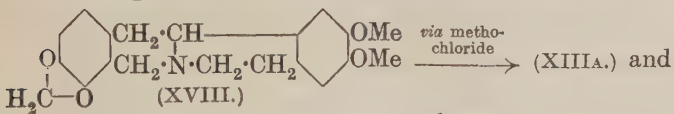
(XVI.)



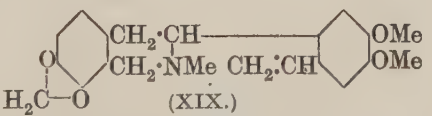
(XVII.)



The latter was reduced to tetrahydro*epi*berberine [2] (XVIII), which, on methylation and treatment of the methiodide by silver chloride, furnished the methochloride. This occurs in two separable, crystalline forms, identical with the α- and β-forms of *iso*dihydrocryptopine chloride, either of which on conversion by the usual method yields a mixture of the anhydro-bases, *viz.*, anhydrodihydrocryptopines-A (XIIIA) and -B (XIX) [3]; the former of these was converted as described above into cryptopine. The synthesis of anhydrodihydroprotopine-A (XIVA) was carried out on analogous lines, the initial condensation being effected between 3 : 4-methylenedioxyhomophthalic acid and β-piperonylethylamine.



(XVIII.) (XIIIA.) and



(XIX.)

All the known di*iso*quinoline alkaloids, natural or synthetic, are

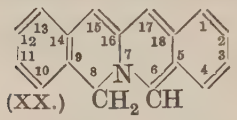
[99] R. D. Haworth and W. H. Perkin, jun., and T. S. Stevens, *J.*, 1926, 1764; **A.**, 951.

[1] Compare this Report, p. 166.

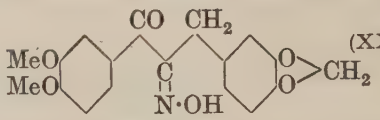
[2] W. H. Perkin, jun., *J.*, 1918, **113**, 518; *A.*, 1918, i, 348.

[3] *Idem, ibid.*, 1916, **109**, 938, 941.

of the " angular " type in structure (see formulæ above) and it is of interest to record the production of the first linear form, for the skeleton (XX) of which the name " paraberine " has been coined.[4] Considerable difficulty was experienced in finding a suitable starting

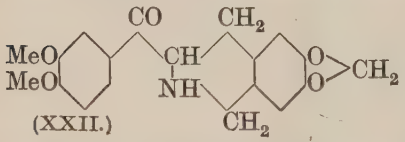


(XX.)

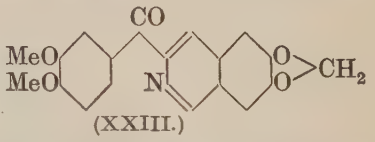


(XXI.)

material, but eventually 3 : 4-dimethoxyphenyl 3 : 4-methylenedioxystyryl ketone was reduced and converted into the *iso*nitroso-derivative (XXI). This, on reduction with stannous chloride under special conditions, gave the corresponding amine, which condensed with formaldehyde to give 6 : 7-methylenedioxy-3-(3′ : 4′-dimethoxybenzoyl)-1 : 2 : 3 : 4-tetrahydro*iso*quinoline (XXII). The latter was

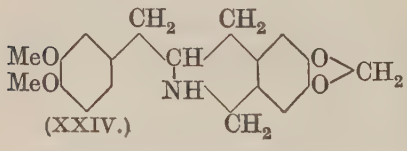


(XXII.)

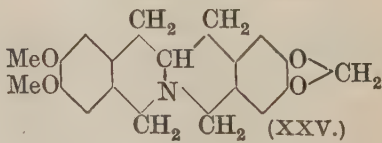


(XXIII.)

oxidised by iodine to the corresponding unreduced *iso*quinoline (XXIII), closely resembling papaveraldine in structure and properties. On reduction of this, the corresponding secondary alcohol, which resembles papaverinol, was formed. By electrolytic reduction in hot dilute sulphuric acid of substance (XXIII), a base (XXIV) corresponding with tetrahydropapaverine was formed and this was converted into 2 : 3-methylenedioxy-11 : 12-dimethoxy-6 : 15 : 16 : 17-tetrahydroparaberine (XXV) by the action of formaldehyde and hydrochloric acid.



(XXIV.)



(XXV.)

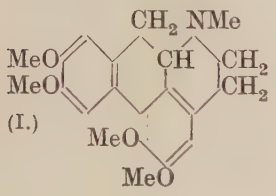
This substance exhibits a general similarity in properties to tetrahydroberberine and its pseudo-isomeride; unlike these, however, it is not oxidised by iodine to the corresponding quaternary iodide (berberinium or ψ-berberinium iodide), but is converted into a crystalline hydriodide of an amorphous base, which is 2 : 3-methylenedioxy-11 : 12-dimethoxy-6 : 17(or 6 : 15)-dihydroparaberine.

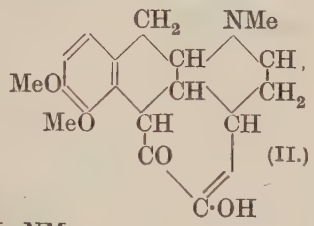
It is suggested that the difficulty of forming such linear structures and the small yields obtained may account for the invariable, so

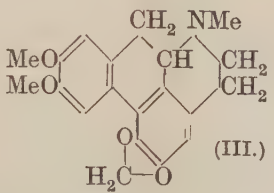
[4] R. Campbell, R. D. Haworth, and W. H. Perkin, jun., *J.*, 1926, 32; **A.**, 303.

far as present knowledge goes, occurrence of the angular forms in nature.

*Phenanthreno*iso*quinolines*.—The alkaloid boldine, which has been known since 1872, is shown to have the formula $C_{19}H_{21}O_4N$. It undergoes the typical reactions of this type of *iso*quinoline alkaloid, furnishing eventually 2 : 3 : 5 : 6-tetramethoxy-8-vinylphenanthrene on "exhaustive methylation." It contains two methoxyl groups and yields a dimethyl ether, which is identical with glaucine (I). Its skeletal structure is therefore certain and it is considered likely that there is one hydroxyl group in each of the rings 1 and 4.[5]







Sinomenine, $C_{19}H_{23}O_4N$, appears to offer an interesting variant on the natural alkaloids of this type in containing a carbonyl group in the fourth ring. It is converted into methylethylamine and sinomenol, $C_{16}H_{14}O_4$, which is regarded as 3 : 4-dihydroxy-5 : 6-dimethoxyphenanthrene, on treatment with 66% potassium hydroxide solution. On this and other grounds it is represented by formula (II).[6] Of the small group of natural alkaloids of this type, only two, *viz.*, glaucine (I) and dicentrine (III), have been synthesised and the latter has now been resolved into its enantiomorphs.[7] The final stage of such syntheses is due to Pschorr [8] and consists in diazotising, in presence of copper, the appropriate 2′-aminobenzyltetrahydro*iso*quinoline, and the way was opened for the preparation of a series of the latter materials with the discovery by E. Hope and R. Robinson [9] that cotarnine and allied bases can be condensed with *o*-nitrotoluene and its derivatives to give *o*-nitrobenzyltetra-

[5] K. Warnat, *Ber.*, 1925, **58**, 2768; 1926, **59**, 85; **A.**, 1926, 185, 311.

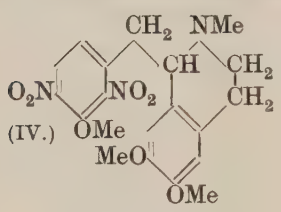
[6] K. Goto, *Proc. Imp. Acad. Tokyo*, 1926, **2**, 7, 167; **A.**, 1160.

[7] R. D. Haworth, W. H. Perkin, jun., and J. Rankin, *J.*, 1926, 29; **A.**, 310; compare *Ann. Reports*, 1925, **22**, 151.

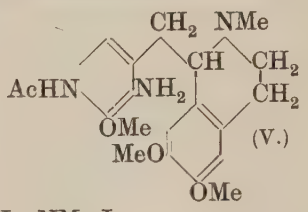
[8] *Ber.*, 1904, **37**, 1926; *A.*, 1904, i, 612.

[9] *J.*, 1911, **99**, 2114.

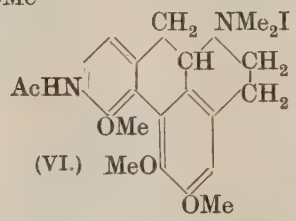
hydro*iso*quinolines. An instance of the application of these two reactions was given last year in the synthesis of aporphine by J. Gadamer, M. Oberlin, and A. Schoeler.[10] In a preliminary investigation of the possibilities of synthesising a series of these alkaloids, R. Robinson and J. Shinoda [11] have condensed laudaline [12] (1-hydroxy-6 : 7-dimethoxy-2-methyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline) with 2 : 4-dinitro-3-methoxytoluene to give the substance (IV), and



(IV.)



(V.)



(VI.)

converted this with difficulty [13] into anhydrolaudaline-2-amino-4-acetamido-3-methoxytoluene (V), from which the methiodide (VI) was prepared by Pschorr's process, followed by treatment with methyl iodide. Replacement of the acetamido-group in this methiodide by hydroxyl should give the methiodide of an alkaloid having one of the formulæ which have been suggested for *iso*corydine.[14]

Morphine Sub-group.—Of the numerous papers published relating to morphine, codeine, and thebaine, the two of most general interest are probably those of J. M. Gulland and R. Robinson [15] and of H. Wieland and M. Kotake [16] in which an approximation to an agreement regarding the formulæ to be assigned to codeine and thebaine is perceptible. On the ground that codeine and the methylmorphimethines show strong evidence of unsaturation,[17] the former authors now adopt formula (I), whilst Wieland and Kotake suggest

[10] *Ann. Reports*, 1925, **22**, 152.

[11] *J.*, 1926, 1987; **A.**, 1048.

[12] F. L. Pyman, *J.*, 1909, **95**, 1266.

[13] Compare R. Robinson and (Miss) H. West, *J.*, 1926, 1985; **A.**, 1045.

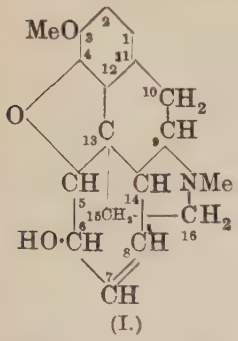
[14] J. Gadamer, *Arch. Pharm.*, 1911, **249**, 503; *A.*, 1911, i, 1011.

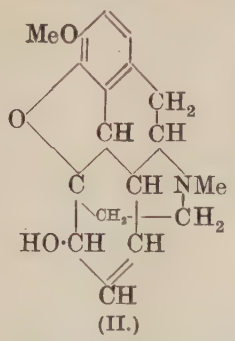
[15] *Mem. Manchester Phil. Soc.*, 1924—25, **69**, 79; **A.**, 1926, 83.

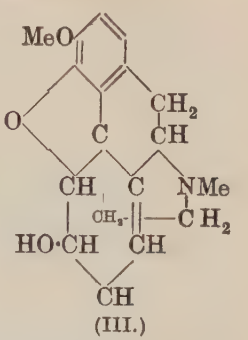
[16] *Annalen*, 1925, **444**, 69; *A.*, 1925, i, 1090; *Ber.*, 1925, **58**, 2009; *A.* 1925, i, 1448.

[17] See, for example, R. S. Cahn and R. Robinson, *J.*, 1926, 908; **A.**, 745, which contains also a discussion of the relative merits of formulæ (I) and (II).

formula (II), which differs from that of Knorr and Horlein [18] only in the removal of the ethylenic linking from C_8–C_{14} to C_7–C_8.


(I.)


(II.)


(III.)

There is, it will be seen, agreement as to the position of the double bond at C_7–C_8 and for different reasons on the part of the two groups of authors, so that the question may be regarded as to that extent simplified. The remaining difference of opinion, the point of attachment of the C_{15} ethanamine chain at C_{13} (G. and R.) or C_5 (W. and K.) requires further experimental evidence for its decision. C. F. van Duin, R. Robinson, and J. C. Smith [19] have shown that neopine, $C_{18}H_{21}O_3N$, one of the rarer alkaloids of opium, is a β-codeine, since on hydrogenation it yields dihydrocodeine, whilst its methosulphate, on warming with potassium hydroxide solution, is converted into β-methylmorphimethine (*see below*). Neopine is therefore represented by formula (III),[20] which differs from codeine (I) only in the transfer of the ethylenic linking from C_7–C_8 to the more protected position C_8–C_{14}.

The relationships of the six methylmorphimethines have been re-investigated by E. Speyer and K. Koulen.[21] These products are formed by the action of caustic alkali on the methiodides of codeine, *iso*codeine, *allo*-ψ-codeine, and ψ-codeine, these bases being themselves monomethyl ethers of morphine and the α-, β-, and γ-*iso*-morphines, respectively. To these must now be added neopine (*see above*), of which the corresponding "morphine" is unknown. Each of these codeine methiodides yields a corresponding methylmorphimethine, some of which are convertible into others by the action of hot alcoholic potassium hydroxide. These points may be summarised thus :

[18] *Ber.*, 1907, **40**, 3341; *A.*, i, 789.

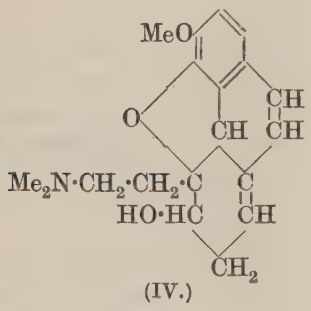
[19] *J.*, 1926, 903; **A.**, 745.

[20] Compare formula (VII) for β-methylmorphimethine (G. and R.).

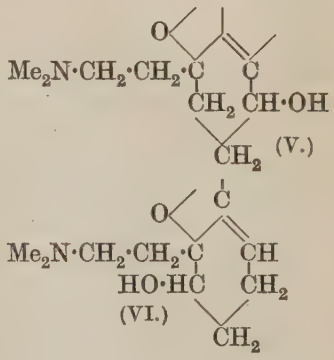
[21] *Annalen*, 1924, **438**, 34; *A.*, 1925, i, 59; compare R. S. Cahn, *J.*, 1926, 2562; **A.**, 1264.

Primary Base	*Methylated Base*	*Methylmorphimethine*
		Primary → *Secondary*
Morphine	Codeine methiodide	α- → β-
α-*iso*—	*iso*—	γ- → δ-
β-*iso*—	*allo*-ψ—	ζ stable to alkali
γ-*iso*—	ψ—	ε—
unknown	β—	β—

The new results indicate that these six methylmorphimethines can be arranged in three groups, α- and γ- being stereoisomeric and represented by formula (IV), ε- and ζ- also are stereoisomerides (formula V), whilst in β- and δ- the ethylenic linking has moved (VI) from C_8–C_{14} to C_{13}–C_{14} (Knorr and Horlein formula). The authors interpret their results on the Knorr and Horlein formula, but in part at least there is no difficulty in transferring them to the more recent formulæ for codeine given above, *e.g.*, β- and δ- methylmorphimethines would, on Gulland and Robinson's formula, be represented by (VII) instead of (VI), whilst from Wieland and Kotake's codeine formula (II) the representation of the β- and δ-methines would probably be (VI).

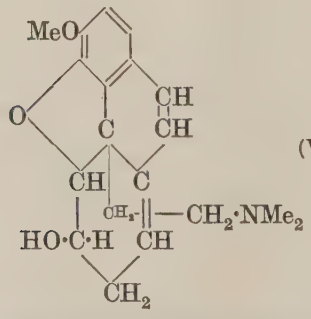


(IV.)



(V.)

(VI.)



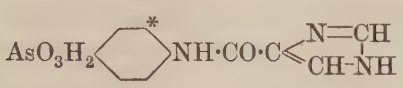
(VII.)

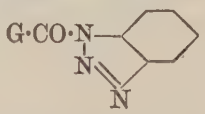
The other papers, far too numerous to mention here, on alkaloids of this sub-group represent a large amount of work, often laborious

and not specially fruitful, but which has added much to our knowledge of these interesting substances.

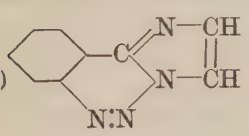
Diazoles.

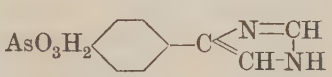
Glyoxalines.—Among the more interesting organic arsenical compounds prepared recently are glyoxaline-4′(or 5′)-carboxy-*p*-aminophenylarsinic acid (I), and its 3-amino-derivative (NH_2 at *), prepared by the application of the Bart–Schmidt reaction to glyoxaline-4(or 5)-carboxy-*p*-aminoanilide and the corresponding amino-derivative.[22] The isomeric *o*-compound does not couple with

(I.) 


(II.)

sodium arsenite because treatment with nitrous acid gives rise to a sparingly soluble, crystalline diazoimide (II, G = glyoxaline nucleus). 2-*m*- and 2-*p*-Aminophenylglyoxalines also were prepared and submitted, under a variety of experimental conditions, to the Bart–Schmidt reaction, but no arsinic acid was formed, and it is suggested that in such cases the conditions favourable for the reaction are also those in which the glyoxaline nucleus can couple with the diazotised base, leading to the formation of insoluble azo-compounds. 2-*o*-Aminophenylglyoxaline yields a small amount of the triazine (III), whilst 4-*p*-aminophenylglyoxaline gives a very small yield of

(III.) 


(IV.)

4-phenylglyoxaline-*p*-arsinic acid (IV). A triazine analogous in structure with (III) was obtained from 4-*o*-aminophenylglyoxaline. The latter was not resolvable into enantiomorphs through the normal *d*-tartrate or the dicamphor-10-sulphonate, an observation of interest in connexion with the current discussion on the representation of diphenyl. So far it has not been possible to introduce arsenic directly into the glyoxaline nucleus.[23]

The determination of the nature of the orienting influence in the nitration of the phenylglyoxalines and their derivatives is still engaging attention.[24]. As a result of a comparative study of the nitration of the benzamidines [25] and phenylpyridines,[26] it is con-

[22] I. E. Balaban and H. King, *J.*, 1925, **127**, 2701; **A.**, 1926, 187.
[23] *Loc. cit.* and I. E. Balaban, *J.*, 1926, 569; **A.**, 623.
[24] Compare *Ann. Reports*, 1924, **21**, 148; 1925, **22**, 156.
[25] R. Forsyth, V. K. Nimkar, and F. L. Pyman, *J.*, 1926, 800; **A.**, 611.
[26] R. Forsyth and F. L. Pyman, *ibid.*, p. 2912.

sidered that in 2-phenylglyoxaline (I) (*p*-nitration predominant) the directive factor is the glyoxalinium ion as a whole, which behaves as an aromatic complex and exerts a para-directive influence like the phenyl group in diphenyl. In 2-phenyl-4 : 5-dihydroglyoxaline (II) (*m*-nitration predominant), it is suggested that the aromatic character of the glyoxaline nucleus is lost and that the meta-directive influence is exerted by the amidinium ion, also present in the salts of benzamidine and benzenyltrimethylamidine (III), which similarly nitrate mainly in the *m*-position. In the special case of 2-phenylglyoxaline-4 : 5-dicarboxylic acid (*m*-nitration predominant), it is believed that the change in directive influence may be due either to a difference in the influence of glyoxaline " base " and " ion," the dicarboxylic acid being non-salt-forming, or to the accumulation of acidic groups, since in the monocarboxylic acid *p*-nitration, although less than in 2-phenylglyoxaline, is still predominant, just as in the series benzyl chloride, benzylidene chloride, and benzotrichloride there is a progressive change from para- to meta-nitration.[27] The case of 4 : 5-dibromo-2-phenylglyoxaline, however, lends no support to this view, since it gives 63% of *p*-nitro-compound and only 1·8% of an unidentified isomeride.

(I.) $\begin{matrix}CH\cdot NH\\ \|\\ CH{-}N\end{matrix}\!\!>\!CPh$ (II.) $\begin{matrix}CH_2\cdot NH\\ |\\ CH_2{-}N\end{matrix}\!\!>\!CPh$ $\begin{matrix}NMe_2\\ NMe\end{matrix}\!\!>\!CPh$ (III.)

Hydantoins.—The additions to the literature on this subject during the last three years have been largely concerned with the synthesis of new species. Many of these products have been prepared with a view to testing their pharmacological action, but much useful information on the formation and reactions of these substances has also been obtained. An interesting example is that afforded by the synthesis of glutathione [28] in which di(hydantoin-propionyl)cystine is an important intermediate. H. Biltz and K. Slotta [29] have described a method for the synthesis of hydantoins, depending upon the conversion, by the action of potassium cyanate, of aminoacetonitriles [30] into hydantoic acid nitriles (I), followed by simultaneous hydrolysis and ring closure with hydrochloric acid to the hydantoin (II).

(I.) $CRR'(CN)\cdot NR''\cdot CO\cdot NH_2 \longrightarrow \begin{matrix}CRR'{-}NR''\\ |\quad\ |\\ CO\cdot NH\cdot CO\end{matrix}$ (II.)

Although the supposed stereoisomeride of ethyl 4-*p*-anisylidene-hydantoin-3-α-propionate turns out to be actually ethyl 4-*p*-anisylidenehydantoin-1-acetate, the same investigators have been able to

[27] A. F. Holleman, *Rec. trav. chim.*, 1914, **33**, 1; *A.*, 1914, i, 513.
[28] Compare *Ann. Reports*, 1925, **22**, 104.
[29] *J. pr. Chem.*, 1926, [ii], **113**, 233; **A.**, 1045.
[30] N. D. Zelinsky and G. Stadnikov, *Ber.*, 1908, **41**, 2061; *A.*, 1908, i, 607.

demonstrate the existence of two forms of the 1 : 3-disubstitution products of both benzylidene- and anisylidene-hydantoins. The absence of stereoisomerism in the former is assumed to be due to tautomerism, by which the double linking responsible for stereoisomerism may become saturated.

$$CO<\begin{matrix}NH\cdot CO\\ NH\cdot C:CHR\end{matrix} \longrightarrow CO<\begin{matrix}NH\cdot CO\\ N=C\cdot CH_2R\end{matrix}$$

The isomeride of lower melting point is invariably transformed into that of higher melting point by boiling alcoholic hydrogen chloride, but the reverse change has been effected only in one case, *viz.*, 1 : 3-dimethyl-4-anisylidenehydantoin,[32] and then only in small amount by the action of alkali : both forms yield the same 1 : 3-dimethylanisylhydantoin on reduction.[31] The lævo-forms of 2-thio-5-methyl- and 1-benzoyl-2-thio-5-methyl-hydantoins have been prepared [32] by T. B. Johnson's method [33] from *l*-alanine and benzoyl-*l*-alanine. Alkali causes racemisation in both cases, due to enolisation. In the case of the benzoyl derivative, two equivalents of alkali are necessary, as the first merely produces a salt without disturbance of the centre of asymmetry.

$$\begin{matrix}CHMe\cdot NBz\\ CO\text{——}NH\end{matrix}>CS \longrightarrow \begin{matrix}CHMe\cdot NBz\\ CO\text{——}N\end{matrix}>C\cdot SK \longrightarrow \begin{matrix}CMe\text{–}NBz\\ C(OK)\text{–}N\end{matrix}>C\cdot SK$$

Pyrazoles.—H. J. Backer and W. Meijer [34] find that in the preparation of pyrazolones by the action of hydrazine on ketonic esters the first product is a 5-hydroxy-5-alkyloxydihydropyrazole (I),

$$\text{(I.)}\quad \begin{matrix}CMe\cdot CH_2\\ N\text{——}NH\end{matrix}>C(OH)\cdot OR$$

which may then lose either alcohol, producing the pyrazolone, or water, forming an alkyloxypyrazole. The latter have long been known as by-products of the reaction [35] and the yield can be increased to from 20 to 30% by using a concentrated solution of hydrazine hydrochloride in methyl or ethyl alcohol.

The 5-alkyloxypyrazoles described are readily nitrated in position 4, except when the latter is occupied as in the 5-alkyloxy-4-alkylpyrazoles.

Although Rosenmund's method for the preparation of aldehydes

[31] D. A. Hahn and E. Gilman, *J. Amer. Chem. Soc.*, 1925, **47**, 2941, 2953; **A.**, 1926, 180, 181; compare E. P. Carr and M. A. Dobbrow, *ibid.*, p. 2961; **A.**, 180.

[32] B. Sjollema and L. Seekles, *Rec. trav. chim.*, 1926, **45**, 232; **A.**, 414.

[33] *J. Biol. Chem.*, 1912, **11**, 97; *A.*, 1912, i, 390; *Amer. Chem. J.*, 1913, **49**, 69, 197; *A.*, 1913, i, 203, 399; *J. Amer. Chem. Soc.*, 1913, **35**, 1130; *A.*, 1913, i, 1104.

[34] *Rec. trav. chim.*, 1926, **45**, 82, 428; **A.**, 305, 741.

[35] L. Wolff, *Ber.*, 1904, **37**, 2827; *A.*, 1904, i, 722.

by reduction of acid chlorides cannot be applied to 3-methyl-, 4-bromo-3-methyl-, or 4-methyl-pyrazole-5-carboxylic acid or to 3 : 5-dimethyl- or 3-phenyl-5-methyl-pyrazole-4-carboxylic acid, as all these undergo dehydration on treatment with thionyl chloride, it can be used for the 1-methyl derivatives of these acids and the analogous derivatives of pyrazole-3-carboxylic acid, but the yields are small.[36]

Several long papers on isomeric relationships in the pyrazole series have appeared, but these are concerned mainly with experimental details and there is nothing of importance to add to the summary given last year, beyond the new points that (*a*) alkylation of ethyl 5-methylpyrazole-3-carboxylate, followed by elimination of the carboxyl group, leads to the production of both 1 : 3- and 1 : 5-dialkylpyrazoles, (*b*) alkylation of pyrazolecarboxylic acids invariably gives rise to two isomeric acids, where two are theoretically possible, and (*c*) direct alkylation of 3(5)-methylpyrazole produces both 1 : 3- and 1 : 5-dialkyl derivatives.[37]

Indazoles.—The preparation of a considerable number of new indazole derivatives has been described, among which may be mentioned a series of indazyl-fatty acids. The latter were obtained by the action of the ethyl ester of the appropriate bromo-acid on indazole, the acid residue entering the latter in position 2 at temperatures ranging from 100° to 120° and also in position 1 in varying amounts at higher temperatures. In presence of alkali alkyloxide both isomerides are invariably formed. The two indazylacetic acids furnish the corresponding 1- and 2-methylindazoles by decarboxylation, when distilled under reduced pressure, but indazyl-β-propionic acid on similar treatment gives indazole and acrylic acid. In the case of ethyl α-bromo*iso*butyrate, the product of the primary reaction is 2-ethylindazole, due, it is thought, to hydrolysis of the ester by the hydrobromic acid formed in the initial stages followed by alkylation of the indazole by the ethyl bromide produced.[38]

L. F. Fieser [39] has submitted 6-nitroindazole to a number of reactions with a view to comparing the behaviour of heterocyclic systems with benzene, without detecting any marked differences. Further, comparison of the reduction potential of sodium 6 : 7-indazolequinone-4-sulphonate with that of potassium β-naphthaquinone-4-sulphonate, in buffer solutions over a wide range of p_H,

[36] C. A. Rojahn and H. E. Kühling, *Arch. Pharm.*, 1926, **264**, 337; **A.**, 846; compare *Ann. Reports*, 1924, **21**, 149.

[37] K. von Auwers with H. Hollmann, *Ber.*, 1926, **59**, 601, 1282; with H. Mauss, *ibid.*, p. 611; with H. Stuhlmann, *ibid.*, p. 1043; **A.**, 623, 624, 741, 847; compare C. A. Rojahn and H. E. Kühling, *Ber.*, 1926, **59**, 607; **A.**, 624.

[38] K. von Auwers and H. G. Allardt, *Ber.*, 1926, **59**, 95; **A.**, 307.

[39] *J. Amer. Chem. Soc.*, 1926, **48**, 1097; **A.**, 625.

gave average values 0·620 and 0·630 volt, indicating a close relationship between the benzene and pyrazole rings.

If, as already suggested,[40] the supposed 1-acetylindazole is really the seven-membered ring substance 4 : 5-benzo-7-methylhept-1 : 2 : 6-oxdiazine (I), then the similarly produced "1-acetyl-3

(I.) $C_6H_4<\begin{matrix}C(OH):N\\N=CMe\end{matrix}>O$ $C_6H_4<\begin{matrix}CMe:N\\N:CMe\end{matrix}>O$ (II.)

methylindazole" (II) (4 : 5-benzo-3 : 7-dimethylhept-1 : 2 : 6-oxdiazine) should not be readily oxidised.[41] This is found to be the case as regards perbenzoic acid; with potassium permanganate, however, it yields *o*-acetamidoacetophenone, and the formation of this is not readily explained on anything but the oxdiazine formula. It was not found possible to prepare "1-benzoylindazole" from *o*-chlorobenzaldehydebenzoylhydrazine by ring closure with sulphuric acid, but the halogen atom of the 2-chloro-5-nitro-derivative proved more mobile and by the use of potassium carbonate, copper powder, and potassium iodide in boiling cumene, 4-nitro-1-benzoylindazole was produced, identical with that of K. von Auwers and K. Schwegler.[42] The supposed 1-acetylindazole being disposed of, K. von Auwers and H. G. Allardt[43] have continued their investigation of the other two and, by a study of the addition of acetyl iodide to (*a*) 2-methylindazole and (*b*) 1-methylindazole, have come to the conclusion that the primary additive products are represented by formulæ (III) and (IV) respectively, since the former is decom-

(III.) $\left[C_6H_4<\begin{matrix}CH\\NAc\end{matrix}>NMe\right]I$ $\left[C_6H_4<\begin{matrix}CH\\NMe\end{matrix}>NAc\right]I$ (IV.)

posed by water into 2-methylindazole and the stable acetylindazole, m. p. 41°, which is now regarded as 1-acetylindazole (formerly called stable 2-acetylindazole); it regenerates (III) when treated with methyl iodide. The second additive product (IV) on treatment with water forms 1-methylindazole and acetic acid, the non-appearance of the expected 2-acetylindazole, m. p. 106° (formerly called labile 2-acetylindazole), being due to the instability of the latter. This isomeride does not react with methyl iodide at atmospheric temperature and decomposes when heated, so that it has not been possible to form the additive product (IV) by the inverse method.

This discussion is extended by K. von Auwers and E. Frese[44] to

[40] See *Ann. Reports*, 1924, **21**, 150.

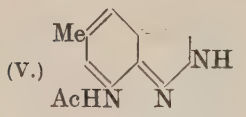
[41] J. Meisenheimer and O. Senn, *Ber.*, 1926, **59**, 199; **A.**, 414.

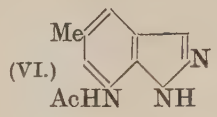
[42] *Ibid.*, 1920, **53**, 1211; *A.*, 1920, i, 640.

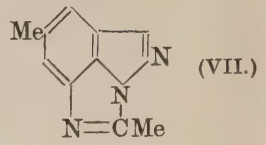
[43] *Ibid.*, 1926, **59**, 90; **A.**, 306; compare *Ann. Reports*, 1924, **21**, 150; 1925, **22**, 162.

[44] *Ber.*, 1926, **59**, 539; **A.**, 529.

the monoacetyl derivatives of 7-amino-5-methylindazole, of which two forms have been obtained, represented by formulæ (V) and (VI),







derived, respectively, from the labile 7-acetamido-2-acetyl-5-methylindazole and the stable 7-acetamido-1-acetyl-5-methylindazole. Of the latter two, the first is formed from the parent base by the action of acetic anhydride at 100° and is converted into the second by distillation under reduced pressure. Analogous di- and monobenzoyl derivatives were also obtained. Prolonged ebullition of 7-amino-5-methylindazole with acetic anhydride gives rise to a triacetyl derivative instead of the expected anhydro-base (VII), and, similarly, anhydro-bases could not be obtained from either the mono- or the di-acetyl derivative by the use of various dehydrating agents. Further, it was not found possible to prepare an anhydro-base from 7(4)-amino-2-methylbenziminazole by the use of either acetic acid or anhydride and this method of converting *o*-diamines into anhydro-bases appears not to be capable of general application.

Diazines.

Pyrazine Derivatives.—According to J. von Braun, O. Goll, and F. Zobel,[45] the piperazine ring (hexahydropyrazine) is a very unstable structure, the replacement of the 4-methylene group of the piperidine by the imino-group causing much greater weakness than its replacement by oxygen as in morpholine. Thus the action of ammonia on piperazinedipiperidinium bromide leads to fission exclusively in the piperazine ring. With cyanogen bromide, dimethylpiperazine furnishes methylvinylcyanamide and methyl-β-bromoethylcyanamide. Similarly, when piperazinebisdihydro-*iso*indolinium bromide (I) is treated successively with silver oxide and boiling water, it is the piperazine ring which is opened, leaving

(I.) $C_6H_4<\begin{matrix}CH_2\\CH_2\end{matrix}>NBr<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>NBr<\begin{matrix}CH_2\\CH_2\end{matrix}>C_6H_4$

(II.) $\left[C_6H_4<\begin{matrix}CH_2\\CH_2\end{matrix}>N\cdot CH_2\cdot\right]_2$

αβ-bisdihydro*iso*indylethane (II). The corresponding piperazine-ditetrahydro*iso*quinolinium bromide under like conditions yields αβ-di-2-tetrahydro*iso*quinolylethane and 2-β-hydroxyethyltetra-

[45] *Ber.*, 1926, **59**, 936; **A.**, 739.

hydro*iso*quinoline along with some acetaldehyde and tetrahydro*iso*-quinoline.

On treatment with methyl iodide, piperazine yields first 1 : 4-dimethyl- and then 1 : 1 : 4 : 4-tetramethyl-piperazine. Similarly, 2 : 5-dimethylpiperazine yields first the 1 : 2 : 4 : 5-tetramethyl derivative and finally 1 : 1 : 2 : 4 : 4 : 5-hexamethylpiperazine.[46]

C. Stoehr [47] showed that 2 : 5-dimethylpyrazine on reduction with sodium in alcohol produces two stereoisomeric forms (α and β) of 2 : 5-dimethylpiperazine. The β-form, like the α-form, has now been resolved into its enantiomorphs and the two are shown to be respectively *trans*- and *cis*-forms. They are produced in the proportion 19 : 1 in the initial reduction.[48] Enolic forms of various 2 : 5-diketopiperazines have been obtained and have been the subject of interesting biological speculations.[49]

Pyrimidines.—Previous investigation having shown that glyoxalines (cyclic amidines) and open-chain amidines yield on methylation mixtures of isomeric *N*-methyl derivatives,[50] the work has been extended [51] to the partly cyclic amidine, 4-anilino-2-phenyl-6-methylpyrimidine (I).

(I.) PhC$\begin{matrix}\diagup\!\!\diagdown \text{N}\!=\!\!=\!\!=\text{CMe}\diagdown\!\!\diagup \\ \text{N·C(NHPh)}\end{matrix}$CH PhC$\begin{matrix}\diagup\!\!\diagdown \text{N}\!=\!\!=\!\!=\text{CMe}\diagdown\!\!\diagup \\ \text{N·C(NMePh)}\end{matrix}$CH (II.)

This yielded a methiodide, m. p. 220°, in which the second methyl group must be either at *N* 1 or 3 in the pyrimidine ring, since on treatment with alkali it yields, not the colourless base represented by (II), but a yellow, unstable base which must be either 4-phenylimino-2-phenyl-3 : 6-dimethyl-3 : 4-dihydropyrimidine (III) or the 1 : 6-dimethyl isomeride of this (IV).

(III.) PhC$\begin{matrix}\diagup\!\!\diagdown \text{N}\!-\!\!-\!\!-\text{CMe}\diagdown\!\!\diagup \\ \text{NMe·C(:NPh)}\end{matrix}$CH PhC$\begin{matrix}\diagup\!\!\diagdown \text{NMe}\!-\!\text{CMe}\diagdown\!\!\diagup \\ \text{N·C(:NPh)}\end{matrix}$CH (IV.)

This on further methylation furnishes a product which is identical with that obtained on methylation of (II) and must be 4-methylanilino-2-phenyl-3 : 6(or 1 : 6)-dimethylpyrimidinium iodide (V =

[46] E. Abderhalden and R. Haas, *Z. physiol. Chem.*, 1925, **148**, 245; **149**, 94; **A.**, 1926, 79, 181.

[47] *J. pr. Chem.*, 1893, [ii], **47**, 439; 1897, [ii], **55**, 49; *A.*, 1893, i, 486; 1897, i, 298.

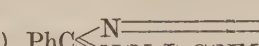
[48] F. B. Kipping and W. J. Pope, *J.*, 1926, 1076; **A.**, 739; compare W. J. Pope and J. Read, *J.*, 1912, **101**, 2325; 1914, **105**, 219.

[49] E. Abderhalden and co-workers, *Z. physiol. Chem.*, 1925, **149**, 100, 298; 1926, **152**, 88; **153**, 83; **155**, 195, 200; **157**, 140; **A.**, 181, 306, 630, 740, 959, 960.

[50] F. L. Pyman, *J.*, 1923, **123**, 367, 3359 and *Ann. Reports*, 1924, **21**, 147; 1925, **22**, 156.

[51] R. Forsyth and F. L. Pyman, *J.*, 1926, 2502; **A.**, 1156.

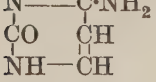
3 : 6 form). In the original methylation, the second iodide, m. p. 182—183°, formed proved to be a molecular mixture of (V) with the

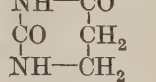
(V.) 

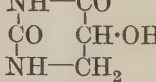
original base (I). Substance (V) on distillation yields the methylanilino-base (II).

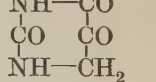
These results are in harmony with those obtained by the application of methyl salts to those partly cyclic amidines which contain one of their nitrogen atoms as a member of an aromatic nucleus, such as the suitably substituted thiazoles,[52] 2-aminopyridine [53] and 1-aminobenzthiazole.[54] The reason for this preferential methylation of the ring nitrogen atom is probably not the weaker basicity of this nitrogen atom but the general structure of the molecule, partly cyclic amidines of the type now discussed tending to react in the form in which the cyclic nitrogen is doubly linked, that is, as amino-derivatives of aromatic compounds rather than as the isomeric iminodihydro-derivatives.

Among a considerable number of interesting observations on uracil, thymine, cytosine, and other pyrimidine derivatives, reference may be made to the isolation of 5-methylcytosine from the hydrolytic products of the nucleic acid of *Bacillus tuberculosis* [55] and to work from the same laboratory on the reduction of cytosine (I) by hydrogen in presence of colloidal platinum. The products are hydrouracil (II) and ammonia. With 5-nitrouracil, 5-amino-


(I.)


(II.)


(III.)


(IV.)

uracil is first formed and then partly hydrolysed first to 5-hydroxyuracil (*iso*barbituric acid) and finally to a new substance, to which formula (III) or (IV) is assigned.[56]

H. Biltz and T. Köhler [57] have produced what appears to be satisfactory evidence that 5-benzoylbarbituric acid (V) is formed when barbituric acid is treated with benzoic anhydride and that the acyl group also takes up the same position in the 1 : 3-dialkyl-

[52] G. Young and S. I. Crookes, *J.*, 1906, **89**, 59.

[53] A. E. Tschitschibabin and R. A. Konowalowa, *Ber.*, 1921, **54**, 814; *A.*, 1921, i, 450.

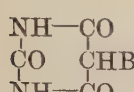
[54] R. F. Hunter, *J.*, 1926, 1385; **A.**, 849.

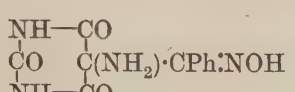
[55] T. B. Johnson and R. D. Coghill, *J. Amer. Chem. Soc.*, 1925, **47**, 2838; **A.**, 1926, 79.

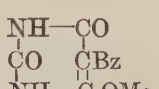
[56] E. B. Brown and T. B. Johnson, *ibid.*, 1924, **46**, 702; *A.*, 1924, i, 567.

[57] *Ber.*, 1923, **56**, 2482; *A.*, 1924, i, 210.

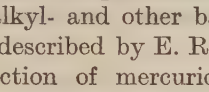
barbituric acids. With hydroxylamine, it yields the oxime of 5-amino-5-benzoylbarbituric acid (VI), and it is converted by methyl sulphate in presence of alkali into the methyl ether of the enolic form (VII). A similar study has been made of 5-nitrobarbituric acid.[58]

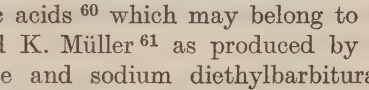

(V.)


(VI.)


(VII.)

The ingenuity of inventors in finding new variants of alkyl-barbituric acids for use as hypnotics shows little diminution and in this connexion mention may be made of an attempt to correlate structure with therapeutic action in this group.[59] P. Fleury has described in a preliminary fashion a number of mercury derivatives of dialkyl- and other barbituric acids [60] which may belong to the type described by E. Rupp and K. Müller [61] as produced by the interaction of mercuric acetate and sodium diethylbarbiturate. Here a precipitate is first formed of the acetoxymercuri-derivative

(VIII.) 


(IX.)

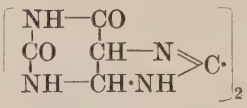
(VIII), and the filtrate from this, on further treatment with the organic component, gives the more complex mercury compound (IX).

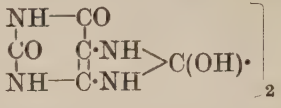
Purine Group.

In this group, a considerable number of syntheses have been effected, especially by H. Biltz and his co-workers.[62] Among these may be mentioned that of 5-amino-4-hydroxy-4 : 5-dihydrouric acid,[63] which is converted by nitrogen trioxide into the corresponding uric acid glycol. The stability of these two substances towards various reagents has been studied in comparison with that of the corresponding ψ-uric acid derivatives. H. Wieland and C. Schöpf [64] have isolated yellow (xanthopterin) and white (leucopterin) pigments

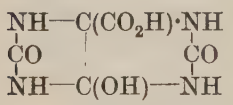
[58] H. Biltz and K. Sedlatscheck, *Ber.*, 1924, **57**, 339; *A.*, 1924, i, 429.
[59] A. W. Dox, *J. Amer. Pharm. Assoc.*, 1923, **12**, 602; *A.*, 1924, i, 668; *J. Amer. Chem. Soc.*, 1924, **46**, 2843; *A.*, 1925, i, 301.
[60] *Bull. Soc. chim.*, 1925, [iv], **37**, 1656; 1926, [iv], **39**, 99; **A.**, 305, 420.
[61] *Arch. Pharm.*, 1926, **264**, 362; **A.**, 852.
[62] *Ber.*, 1924, **57**, 175; 1925, **58**, 2190; *A.*, 1924, i, 431; 1925, i, 1462
[63] H. Biltz and W. Klemm, *Annalen*, 1926, **448**, 134; **A.**, 962.
[64] *Ber.*, 1925, **58**, 2178; 1926, **59**, 2067; *A.*, 1925, i, 1464; **A.**, 1926, 1168.

from the wings of lemon and white butterflies and suggest that these may be represented by the following formulæ, respectively :

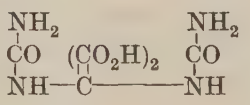




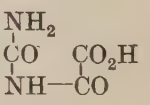
Much attention has been directed during the last three years to attempts to determine the mechanism of oxidation of uric acid and its derivatives. With a variety of agents tried in acid, neutral, or buffer solutions by H. Biltz and H. Schauder,[65] oxaluric acid (III) is the most constant product, and, although it can arise from such possible intermediates as uric acid glycol, alloxan, or allantoin, the experimental evidence supports, but does not clearly establish, the view that it comes from the hypothetical hydroxydicarbamidoethanecarboxylic acid (I), for which the names hydroxyacetylenediureinecarboxylic acid and hydroxyglycolurilcarboxylic acid also have been used.



(I.)

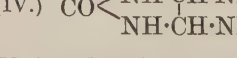


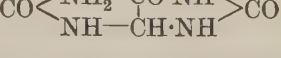
(II.)



(III.)

This has already been postulated as the precursor of uroxanic acid (II), obtained when uric acid is oxidised in alkaline solutions,[66] and it is now suggested that during oxidation in acid or neutral solutions, uroxanic acid is not formed because under these conditions carbon dioxide is spontaneously lost from hydroxydicarbamidoethanecarboxylic acid (I). All attempts to isolate the latter have failed, but in suitably oxidised uric acid solutions its presence is regarded as proved since, by acidification with acetic acid followed by reduction with sodium amalgam, dicarbamidoethane (IV) (acetylenediureine) is obtained. This substance is also produced when allantoin

(IV.) 



(V.)

(V) is reduced under similar conditions in presence of sulphuric acid. In this case, reduction is believed to precede ring formation, and this is regarded as further evidence for the monocyclic structure (V) of allantoin.[67] A general discussion of the breakdown of uric acid

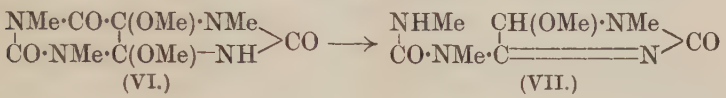
[65] *J. pr. Chem.*, 1923, [ii], **106**, 108; *A.*, 1924, i, 569.

[66] R. Berend, *Annalen*, 1904, **333**, 141; *A.*, 1904, i, 950; compare H. Biltz and F. Max, *Ber.*, 1920, **53**, 1964; *A.*, 1920, i, 884.

[67] H. Biltz and G. Schiemann, *J. pr. Chem.*, 1926, [ii], **113**, 77; **A.**, 741; compare H. Biltz and F. Max, *Ber.*, 1921, **54**, 2451; *A.*, 1921, i, 893, and H. Biltz and H. Hanisch, *J. pr. Chem.*, 1926, [ii], **112**, 138; **A.**, 414.

glycols and their degradation products has been published by K. H. Slotta.[68]

The smooth conversion of 4 : 5-dimethoxy-4 : 5-dihydrouric acid (uric acid glycol dimethyl ether) into allantoin (V) by potassium hydroxide appears to be exceptional, since allantoins are either not formed or are produced in minute quantity by the action of alkalis on other uric acid glycol ethers. Thus, in the glycol ethers containing a methyl group in position 3 in the pyrimidine ring, fission occurs between positions 1 and 6, methylamine, cyanic acid, and carbon dioxide are lost, and a substituted hydantoin is formed,[69] although disruption may be less complete than this, as with 1 : 3 : 7-trimethyluric acid glycol dimethyl ether (VI) which, on treatment with 30% potassium hydroxide solution, gives 4-*s*-dimethylcarbamido-5-methoxy-1-methyl-Δ^3-glyoxal-2-one (VII).



(VI.) (VII.)

T. A. Henry.

[68] K. H. Slotta, *J. pr. Chem.*, 1925, [ii], **110**, 264; *A.*, 1925, i, 1189.

[69] H. Biltz and H. Klein, *Ber.*, 1925, **58**, 2740; **A.**, 1926, 182. For a similar study of the action of alkalis on alkyluric acids, see E. S. Gatewood, *J. Amer. Chem. Soc.*, 1923, **45**, 3056; 1925, **47**, 2175, 2181; *A.*, 1924, i, 218; 1925, i, 1188, 1189. Compare L. Piaux, *Bull. Soc. chim.*, 1925, [iv], **37**, 311; 1926, [iv], **39**, 1471; *A.*, 1925, i, 592; **A.**, 1926, 1261.

ANALYTICAL CHEMISTRY.

THERE is little of entirely novel character to report in analytical chemistry during the year under review. Several improvements and advances in potentiometric and conductometric determinations have been recorded. The difficulties attaching to many of the processes of estimating and detecting substances by the ordinary methods are again discussed and examined in detail. Microchemical determinations are likewise being actively investigated, with a considerable measure of success. Some attention has been directed to the separations of the rarer alkali metals and a useful modification of the bleaching method for the colorimetric determination of fluorine has been described. We have, in this Report, given a *résumé* of the more important methods for the estimation of large and of small quantities of fluorine (excluding the well-known silicon fluoride method), since the accurate determination of this element is becoming of increasing importance in many directions.

Inorganic Analysis.

Qualitative.—The methods previously described [1] for the rapid and ready detection of certain metals by use of drops of the solutions to be tested have now been extended [2] to embrace all the common cations; the scheme avoids the use of hydrogen sulphide. The precipitates produced in solutions of the heavy metals by 36 aliphatic and heterocyclic bases have been studied [3] with a view to the possible application of the results to the separation of various metals. In particular, the violet-blue precipitate yielded by glyoxaline with cobalt constitutes a delicate test for this metal. Diphenylthiocarbazone forms highly-coloured compounds with a number of heavy metals most of which are soluble in chloroform and carbon disulphide. Sensitive and characteristic tests for zinc and copper are based on this reaction.[4]

Traces of silver in ores can be detected by microchemical reactions due to the formation of rubidium silver gold chloride.[5] The form-

[1] N. A. Tananaev, *Z. anorg. Chem.*, 1924, **133**, 372; **140**, 320; *A.*, 1924, ii, 571; 1925, ii, 324.

[2] *Ukraine Chem. J.*, 1926, **2**, 27; **A.**, 927.

[3] E. J. Fischer, *Wiss. Veröff. Siemens-Konz.*, 1925, **4**, 171; **A.**, 1926, 492.

[4] *Ibid.*, p. 158; **A.**, 1926, 491.

[5] W. Geilmann, *Z. anorg. Chem.*, 1926, **155**, 192; **A.**, 1019.

ation of a copious white precipitate on addition of 1% brucine sulphate and potassium bromide to a cadmium solution serves to detect this metal in the presence of copper,[6] and the reaction may be utilised to differentiate between bromides and chlorides. Microscopic examination of the deposit on a copper wire acting as cathode is capable of revealing mercury when present to the extent of only 0·5 mg. per litre.[7]

Aluminium gives with an extract of dried alkanet root a characteristic purple lake when ammonia is added in excess.[8]

Nickel sulphate gives with a large excess of concentrated hydriodic acid an intense red colour similar to that of ferric thiocyanate; this colour disappears on sufficient dilution by water. Characteristic effects on the colour and absorption spectra of solutions of cobalt salts are induced by hydrobromic and hydriodic acids.[9] Solutions of cobaltous salts give with potassium ferrocyanide in the presence of ammonia a red coloration, perceptible in very dilute solutions, and the test is not vitiated by a considerable excess of nickel salts.[10] The sensitiveness of the borax bead test for cobalt can be greatly increased by microscopical examination of minute borax beads.[11]

The sensitivity of a number of reagents for the strontium ion has been worked out; calcium can be detected, after removal of barium and strontium as chromates by prescribed methods, by means of potassium ferrocyanide.[12] Sodium ferrocyanide in the presence of calcium chloride gives a precipitate with aqueous solutions containing rubidium and cæsium; potassium and ammonium are only precipitated from 50% ethyl-alcoholic solution, whilst sodium and lithium are not affected. These reactions afford a means of separating the alkalis.[13] Thallium even in dilute solution also forms a precipitate when calcium acetate is used with sodium ferrocyanide.[14] Complete qualitative separations of the various metals of the alkali group are described in a lengthy paper.[15] Optimum con-

[6] R. Meurice, *Ann. Chim. anal.*, 1926, [ii], **8**, 130; **A.**, 703.

[7] H. S. Booth and N. E. Schreiber, *J. Amer. Chem. Soc.*, 1925, **47**, 2625; **A.**, 1926, 40.

[8] H. W. Estill and R. L. Nugent, *ibid.*, 1926, **48**, 168; **A.**, 263.

[9] G. Denigés. *Compt. rend.*, 1926, **183**, 55; **A.**, 930.

[10] L. Mindalev, *Mitt. wiss.-tech. Arb. Republ.* [*Russ.*], 1924, **13**, 57; **A.**, 1926, 264.

[11] J. Mika, *Koll.-Chem. Beih.*, 1926, **23**, 309; **A.**, 1116.

[12] D. Raquet, *Ann. Chim. anal.*, 1926, [ii], **8**, 3; **A.**, 262.

[13] T. Gaspar y Arnal, *Anal. Fís. Quím.*, 1926, **24**, 99; **A.**, 591; F. Diaz de Rada and T. Gaspar y Arnal, *ibid.*, p. 150; **A.**, 702.

[14] T. Gaspar y Arnal, *ibid.*, p. 153; **A.**, 703.

[15] S. Ato and I. Wada, *Sci. Papers Inst. Phys. Chem. Res.*, 1926, **4**, 263; **A.**, 929.

ditions under which the oxalate test for sodium should be carried out are described; borax is the only common sodium compound which does not respond to this test. Potassium pyroantimonate is a better reagent and may be used in presence of boric acid.[16] The precipitation of sodium magnesium uranyl acetate in the presence of alcohol is of value in the detection of small quantities of sodium in the presence of potassium and magnesium, but is valueless for quantatitive work.[17]

For the microchemical detection of germanium, no characteristic reagent was discovered; the most practicable test was found to depend on the conversion into sodium fluogermanate or rubidium germanomolybdate following a preliminary separation from several elements which normally give positive tests with fluorides and molybdates.[18] In the absence of iron and metals of the first two analytical groups, the coloration given with pyrocatechol indicates the presence of cerium even in minute traces.[19]

The hydrogen peroxide test for titanium is not suitable for spot analysis on filter-paper; for this purpose, the red coloration given by chromotropic acid is most satisfactory. Copper, iron, and titanium interfere with the ferrocyanide spot-test for uranium, but this difficulty may be obviated by reducing the former with potassium iodide and decolorising the iodine with thiosulphate.[20] The lakes formed by "aluminon" (aurintricarboxylic acid) with a number of the rarer metals have been more completely investigated; with the exception of the beryllium lake, all are dissolved or decolorised by ammonium carbonate.[21] Reactions of a number of hydroxyanthraquinone derivatives with zirconium and hafnium are described; the reddish-violet solution obtained in the case of alizarinsulphonic acid is a sensitive reagent for fluorides, which, by converting the zirconium into a complex fluoride, cause the solution to become yellow.[22] As the result of a study of the reactions between vanadic acid, hydrogen peroxide, and sulphuric acid, the best concentration of sulphuric acid for the detection of vanadium by this test has been worked out.[23]

Traces of soluble ruthenium salts may be detected by heating the solution, rendered alkaline with sodium hydroxide, in a current

[16] N. Schoorl, *Pharm. Weekblad*, 1926, **63**, 555; **A.**, 814.
[17] E. Crepaz, *Ann. Chim. Appl.*, 1926, **16**, 219; **A.**, 1019.
[18] E. M. Chamot and H. I. Cole, *Mikrochem.*, 1926, **4**, 97; **A.**, 1019.
[19] L. Fernandes, *Gazzetta*, 1925, **55**, 616; **A.**, 1926, 140.
[20] N. A. Tananaev and G. A. Pantschenko, *Z. anorg. Chem.*, 1926, **150**, 163; **A.**, 377. See also *Ukraine Chem. J.*, 1926, **2**, 43.
[21] A. R. Middleton, *J. Amer. Chem. Soc.*, 1926, **48**, 2125; **A.**, 930.
[22] J. H. de Boer, *Rec. trav. chim.*, 1925, **44**, 1071; **A.**, 1926, 40.
[23] J. Meyer and A. Pawletta, *Z. anal. Chem.*, 1926, **69**, 15; **A.**, 1020.

of chlorine; a brown coloration in an absorbent consisting of aqueous alcohol containing hydrochloric acid indicates ruthenium.[24] Reactions of the platinum metals with a number of typical organic and inorganic compounds have been tabulated,[25] and a scheme for the qualitative separation of these metals has been worked out.[26]

Specific and delicate tests for nitrate and for hydroxylamine based upon conversion into nitrite and application of the diazo-reaction have been described, together with appropriate methods for the preliminary removal of nitrites.[27] A test for iodate, available in the presence of bromate, chlorate, and nitrate, depends upon the liberation of iodine by reaction with thiocyanic acid.[28] The effects produced by salts of cobalt, copper, and mercury serve to distinguish between carbonates and bicarbonates, sulphites and bisulphites.[29] Bromine, liberated by suitable methods from bromides, hypobromites, or bromates, may be detected in very small amounts by the characteristic crystalline precipitate it produces in a solution of *m*-phenylenediamine in 5% sulphuric acid.[30]

Quantitative.—Pyridinium perchlorate may readily be obtained from technical pyridine in a pure state free from homologues, and can be used as an acidimetric standard.[31] Borax or potassium iodate, used under appropriate conditions, is preferred to sodium carbonate for the standardisation of hydrochloric acid.[32] Constant-boiling hydrochloric acid remains unaltered in strength for long periods and is therefore available for dilution for standard solutions.[33] Two studies have been made of the variability of standard sodium thiosulphate solutions.[34] The high results obtained in the titration with thiosulphate of the iodine set free by potassium dichromate in acid solution are stated to be due to liberation of iodine by atmospheric oxygen in the presence of chromic salts; normal values are obtained if the reaction solutions are first boiled and the process carried out in an atmosphere of carbon dioxide.[35]

Methods depending upon the formation of cyanogen halide have

[24] H. Remy, *Z. angew. Chem.*, 1926, **39**, 1061; **A.**, 1219.
[25] S. C. Ogburn, jun., *J. Amer. Chem. Soc.*, 1926, **48**, 2493; **A.**, 1117.
[26] *Idem, ibid.*, p. 2507; **A.**, 1117.
[27] J. Blom, *Ber.*, 1926, **59**, [*B*], 121; **A.**, 375.
[28] J. Bicskei, *Z. anorg. Chem.*, 1926, **151**, 127; **A.**, 375.
[29] T. Gaspar y Arnal, *Anal. Fis. Quim.*, 1926, **24**, 267; **A.**, 928.
[30] C. W. Mason and E. M. Chamot, *Mikrochem.*, 1926, **4**, 145; **A.**, 1220.
[31] F. Arndt and P. Nachtwey, *Ber.*, 1926, **59**, [*B*], 448; **A.**, 525.
[32] I. M. Kolthoff, *J. Amer. Chem. Soc.*, 1926, **48**, 1447; **A.**, 813; *Pharm. Weekblad*, 1925, **63**, 37; **A.**, 1926, 139.
[33] J. A. Shaw, *Ind. Eng. Chem.*, 1926, **18**, 1065; **A.**, 1220.
[34] C. Mayr, *Z. anal. Chem.*, 1926, **68**, 274; **A.**, 814; E. Schulek, *ibid.*, p. 387; **A.**, 1017.
[35] K. Böttger and W. Böttger, *ibid.*, 1926, **69**, 145; **A.**, 1221.

been studied comprehensively and applied to the determination of chloride, bromide, and iodide, alone or in admixture.[36] The titrations of thiocyanic acid, of arsenious acid, and of antimony with potassium bromate have been investigated from the point of view of the optimum acidity; the potentiometric method permits of a wider range and therefore is preferred to the use of methyl-orange.[37]

Extract of blue cabbage, used as an indicator, gives a series of colour changes between p_H 2 and p_H 11, ranging from red through blue (p_H 6·8—7·1) and green (p_H 8) to yellow; it is, however, extremely sensitive to carbon dioxide.[38] An aqueous solution of yatrenum (which consists of an iodohydroxyquinolinesulphonic acid with an equivalent of sodium bicarbonate) is strongly coloured between p_H 1 and p_H 8, with maximum intensity at p_H 4; the possibility of its use, with buffer solutions, as an indicator is discussed.[39] Under special lighting conditions, quinine[40] and umbelliferone[41] may be used as fluorescent indicators. The first is suitable for turbid liquids and both are available for coloured solutions.

Vanadous sulphate is an even more powerful reducing agent than titanous sulphate; whilst the latter maintains its titre in 4*N*-sulphuric acid in a burette exposed to air for 12 hours, vanadous sulphate must be used within 1 hour.[42] Uranous sulphate is a mild reducing agent the solution of which is stable in air. Its preparation and use for the determination of ferric salts are described in detail.[43] Diphenylamine as an internal indicator has been applied in conjunction with reduction by liquid amalgams to the determination of phosphoric acid, ferricyanide, chromic acid, and ferric salts.[44]

"Citarin," the sodium salt of anhydromethylenecitric acid, can be used for the quantitative precipitation of silver and of gold, owing to the liberation of formaldehyde from the hot alkaline solution.[45] Small amounts of silver can be separated as metal from large quantities of lead or copper by boiling the alkaline solution in the presence of glycerol.[46]

[36] R. Berg, *Z. anal. Chem.*, 1926, **69**, 1; **A.**, 1017.
[37] T. Nakazono and S. Inoko, *J. Chem. Soc. Japan*, 1926, **47**, 20; **A.**, 1115.
[38] T. Milobedzki and S. Jajte, *Rocz. Chem.*, 1926, **6**, 177; **A.**, 927.
[39] H. W. van Urk, *Pharm. Weekblad*, 1926, **63**, 685; **A.**, 813.
[40] R. Mellet and A. Bischoff, *Compt. rend.*, 1926, **182**, 1616; **A.**, 813.
[41] R. Robl, *Ber.*, 1926, **59**, [*B*], 1725; **A.**, 1115.
[42] A. S. Russell, *J.*, 1926, 497; **A.**, 592.
[43] G. Vortmann and F. Binder, *Z. anal. Chem.*, 1925, **67**, 269; **A.**, 1926, 263.
[44] K. Someya, *Z. anorg. Chem.*, 1926, **152**, 368, 382, 386; **A.**, 702, 705; see also *Sci. Rep. Tôhoku Imp. Univ.*, 1926, **15**, 399, 417, 426; **A.**, 1116, 1117.
[45] L. Vanino and O. Guyot, *Arch. Pharm.*, 1926, **264**, 98; **A.**, 491.
[46] E. Donath, *Chem.-Ztg.*, 1926, **50**, 222; **A.**, 491.

Lead may be separated from silver as phosphate from slightly ammoniacal tartrate solution, the temperature of precipitation being less than 80° to avoid reduction of the silver; silver may be separated by addition of potassium iodide to the boiling solution.[47] The effect of varying concentrations of hydrochloric acid on the precipitation of cadmium, bismuth, and lead by hydrogen sulphide has been investigated once more and the requisite conditions for direct separation of metals of this group are described.[48]

Suggestions are given to prevent oxidation of cuprous iodide in Winkler's gravimetric method for the determination of copper as cuprous iodide.[49] Benzoin monoxime does not separate copper completely from iron, aluminium, or zinc, its use in this connexion being criticised.[50] The micro-determination of copper by electrolysis and iodometric titration is applied to 0·5 mg. and less.[51]

Bismuth solutions hydrolyse in the presence of bromide and bromate to basic bismuth bromide. This reaction, which is more delicate than that due to hydrogen sulphide, has been applied to the separation of bismuth from zinc, copper, cadmium, and lead.[52] The methods for the complete removal of mercury from solution by deposition on copper and subsequent determination by sublimation have been reinvestigated and placed on a satisfactory basis suitable for large or small quantities.[53] A number of papers deal with the determination of very small quantities of mercury the separation of which is effected by electrolysis on gold and weighing the metallic mercury; conversion into red mercuric iodide serves as a confirmatory test.[54]

In the absence of gold, mercury, selenium, and tellurium, arsenic may be precipitated by stannous chloride and determined as the element, in which form it may be weighed; the results tend to be high.[55] With certain modifications, arsenic may be reduced to

[47] G. Vortmann and O. Hecht, *Z. anal. Chem.*, 1925, **67**, 276; **A.**, 1926, 262; G. Vortmann, *Analyst*, 1926, **51**, 456; **A.**, 1019.

[48] W. Manchot, G. Grassl, and A. Schreeberger, *Z. anal. Chem.*, 1925, **67**, 177; **A.**, 1926, 40; see also S. Krishnamurti, *J.*, 1926, 1549; **A.**, 814.

[49] I. M. Kolthoff and H. A. Kuylman, *Chem. Weekblad*, 1926, **23**, 185; **A.**, 592.

[50] E. Azzalin, *Ann. Chim. Appl.*, 1925, **15**, 373; **A.**, 1926, 140.

[51] N. Schoorl and H. Begemann, *Rec. trav. chim.*, 1925, **44**, 1077; **A.**, 1926, 40; H. B. Dunnicliff and K. Ram, *Kolloid-Z.*, 1926, **38**, 168; **A.**, 376.

[52] L. Moser and W. Maxymowicz, *Z. anal. Chem.*, 1925, **67**, 248; **A.**, 1926, 264.

[53] B. S. Evans and S. G. Clarke, *Analyst*, 1926, **51**, 224; **A.**, 704.

[54] A. Stock and R. Heller, *Z. angew. Chem.*, 1926, **39**, 466; **A.**, 703; A. Stock and E. Pohland, *ibid.*, p. 791; **A.**, 814; H. S. Booth, (Miss) N. E. Schreiber, and K. G. Zwick, *J. Amer. Chem. Soc.*, 1926, **48**, 1815; **A.**, 929.

[55] R. Fridli, *Pharm. Zentr.*, 1926, **67**, 241; **A.**, 591.

element and determined in the presence of selenium.[56] In the Gutzeit test, a freshly-prepared mercuric bromide paper is highly sensitive and preferable to mercuric chloride;[57] the use of glass wool in place of filter-paper and cotton wool in the purifying tube of the Gutzeit or Marsh apparatus considerably lengthens the effective life of the tube.[58] Arsenic acid may be determined by reduction with titanous chloride and back titration with ferric alum.[59]

Iron may be titrated with titanous chloride in the presence of copper by the use of the chromic acid compound of *s*-diphenylcarbohydrazide, which is reduced instantly by cuprous chloride and very slowly by titanous chloride.[60] Iron is quantitatively precipitated under certain conditions from 2*N*-acid solution containing 2% ammonium salt by the addition of an alkali salt of bis-*p*-chlorophenylphosphoric acid; the precipitate is finally converted into hydroxide by treatment with ammonia.[61]

Aluminium can be satisfactorily separated from magnesium, even in the absence of added ammonium salts, by adding ammonia until p_H 7 is reached (blue with bromothymol-blue), but magnesium is carried down if p_H exceeds 7.[62] Chromium salts are completely oxidised to chromic acid by boiling in alkaline solution with lead dioxide, the excess of which is readily removed by filtration.[63] A direct permanganate titration method similar to the Volhard method for chromium[64] and manganese[65] salts, depending upon the use of excess of sodium acetate, has been worked out and is shown to be available in the presence of much iron. The varying factors influencing the oxidation of manganese salts to permanganic acid and the conditions for securing complete oxidation have been studied,[66] and it is shown that sulphuric acid may advantageously be substituted for nitric acid in the determination of manganese by the bismuthate method.[67]

[56] R. Fridli, *Pharm. Zentr.*, 1926, **67**, 369; **A.**, 702.

[57] G. Kemmerer and H. H. Schrenk, *Ind. Eng. Chem.*, 1926, **18**, 707; **A.**, 928.

[58] T. J. Ward, *Analyst*, 1926, **51**, 457; **A.**, 1018.

[59] A. W. Francis, *J. Amer. Chem. Soc.*, 1926, **48**, 655; **A.**, 490.

[60] L. Brandt, *Stahl u. Eisen*, 1926, **46**, 976; **B.**, 752.

[61] F. Zetzsche and M. Nachmann, *Helv. Chim. Acta*, 1926, **9**, 420; **A.**, 705.

[62] A. Lassieur, *Ann. Chim. anal.*, 1926, [ii], **8**, 97; *Compt. rend.*, 1926, **182**, 384; **A.**, 376.

[63] E. Müller and W. Messe, *Z. anal. Chem.*, 1926, **69**, 165; **A.**, 1222.

[64] B. Reinitzer and P. Conrath, *ibid.*, 1926, **68**, 81; **A.**, 492.

[65] *Idem*, *ibid.*, p. 129; **A.**, 705.

[66] A. Travers, *Compt. rend.*, 1926, **182**, 1088; *Ann. Chim.*, 1926, [x], **6**, 56; **A.**, 704.

[67] B. Park, *Ind. Eng. Chem.*, 1926, **18**, 597; **A.**, 704.

The oxalate separation of calcium and magnesium continues to attract attention, and the effective separation is shown to be due to the degree of supersaturation of magnesium oxalate;[68] it is important to note that calcium oxalate is rapidly and quantitatively converted into carbonate by heating in a current of dry carbon dioxide at 675—800°.[69]

The cobaltinitrite method for the determination of potassium is shown to be available in the presence of sulphate and is thus better than the perchlorate in this case; further confirmation that the composition of the precipitate after drying at 100° is $K_2NaCo(NO_2)_6,H_2O$ has been obtained.[70] It has been found advantageous to replace the acetic acid by tartaric acid in preparing the reagent.[71] Determination of the cobalt in the precipitated cobaltinitrite has been applied to the micro-determination of small quantities of potassium,[72] whilst for micro-determination of sodium use is made of the triple nitrite $6NaNO_2,9CsNO_2,5Bi(NO_2)_3$ through electrolytic separation of bismuth.[73]

Rubidium may be precipitated quantitatively as silicotungstate, $Rb_8SiW_{12}O_{42}$, by addition of silicotungstic acid, but in the presence of more than 1% of potassium the precipitate requires further treatment with 1¼% salt solution to remove co-precipitated potassium.[74] Both rubidium and cæsium may be precipitated from the alcoholic solution of their chlorides and weighed as chlorostannates. If the two metals are present together, the cæsium is subsequently separated as a triple chloride with antimony and iron and then converted into and determined as perchlorate. The precipitate formed by the addition of sodium cobaltinitrite to a solution of a rubidium salt contains varying proportions of sodium, but the cæsium salt, precipitated at 80°, is definitely $Cs_3Co(NO_2)_6,H_2O$.[75] Thallium also is quantitatively precipitated at 80° by sodium cobaltinitrite, the product dried at 100—110° having the composition $Tl_2NaCo(NO_2)_6$. In other methods for determination of thallium, the metal is either weighed as element or estimated volumetrically, the thallium being precipitated by a measured excess of potassium

[68] W. M. Fischer, *Z. anorg. Chem.*, 1926, **153**, 62; **A.**, 703.

[69] H. W. Foote and W. M. Bradley, *J. Amer. Chem. Soc.*, 1926, **48**, 676; **A.**, 491.

[70] M. A. Hamid, *Analyst*, 1926, **51**, 450; **A.**, 1019; L. le Boucher, *Anal. Fís. Quím.*, 1925, **23**, 540; **A.**, 1926, 491.

[71] M. Wikul, *Z. anorg. Chem.*, 1926, **151**, 338; **A.**, 491.

[72] M. Delaville and P. Carlier, *Compt. rend.*, 1926, **182**, 701; **A.**, 491.

[73] E. Tschopp, *Helv. Chim. Acta*, 1925, **8**, 893; **A.**, 1926, 39.

[74] P. Freundler and (Mlle.) Y. Ménager, *Compt. rend.*, 1926, **182**, 1158; **A.**, 702.

[75] W. Strecker and F. O. Diaz, *Z. anal. Chem.*, 1925, **67**, 321; **A.**, 1926, 261.

iodide.[76] Thallous salts are quantitatively oxidised by potassium iodate in the presence of a large excess of hydrochloric acid and so determined,[77] or by potassium bromate. Thallic salts may also be titrated potentiometrically with titanous chloride in the presence of ammonium acetate.[78]

The requisite but simple precautions for the accurate determination of uranium gravimetrically as U_3O_8 following precipitation as $(NH_4)_2U_2O_7$ or volumetrically by means of permanganate are discussed.[79] Sodium cacodylate separates uranium from other metals of the iron group. The precipitate is $[(CH_3)_2AsO]_2UO_2$ and may be weighed in this form.[80] Zirconium may be quantitatively separated from all elements except hafnium as insoluble phenylarsinate from a solution containing 10% hydrochloric or sulphuric acid. The precipitate is ignited directly to zirconia. Double precipitation is necessary for the complete separation from thorium, uranium, phosphoric acid, and iron. Thorium phenylarsinate is the only rare-earth salt of the acid insoluble in excess of acetic acid and this is used in the application of this reagent to the analysis of monazite.[81] Zirconium citrate, although soluble in ammonia or citric acid solution, is only sparingly soluble in water, whilst hafnium citrate is readily soluble.[82] Zirconium hydroxide is soluble in ammonium carbonate solution at 70°; this property has been applied to the separation from iron and aluminium. Thorium, if present, accompanies the zirconium.[83] Niobium (columbium) can be determined in the presence of tantalum by reducing it with hydrogen to the tetroxide and ascertaining the increase in weight on ignition; tantalum pentoxide is not reduced. The black colour of the tetroxide is a sensitive qualitative test for niobium.[84]

Palladium may be separated from the other platinum metals and from the commoner metals by means of benzoylmethylglyoxime. Precipitation is carried out in acid solution, with certain precautions if antimony, molybdenum, vanadium, or tungsten is present.[85]

[76] W. Strecker and P. de la Peña, *Z. anal. Chem.*, 1925, **67**, 256; **A.**, 1926, 262.

[77] A. J. Berry, *Analyst*, 1926, **51**, 137; **A.**, 376.

[78] E. Zintl and G. Rienäcker, *Z. anorg. Chem.*, 1926, **153**, 276; **A.**, 703.

[79] G. E. F. Lundell and H. B. Knowles, *J. Amer. Chem. Soc.*, 1925, **47**, 2637; **B.**, 1926, 1016.

[80] E. Isnard, *Bull. Sci. Pharm.*, 1925, **32**, 131.

[81] A. C. Rice, H. C. Fogg, and C. James, *J. Amer. Chem. Soc.*, 1926, **48**, 895; **A.**, 593.

[82] D. H. Drophy and W. P. Davey, *Physical Rev.*, 1925, [ii], **25**, 882; **A.**, 1926, 1117.

[83] R. Lessing, *Z. anal. Chem.*, 1925, **67**, 341; **A.**, 1926, 263.

[84] O. Ruff and F. Thomas, *Z. anorg. Chem.*, 1926, **156**, 213; **A.**, 1222.

[85] J. Hanuš, A. Jilek, and J. Lukas, *Chem. News*, 1925, **131**, 401; 1926, **132**, 1; *Chem. Listy*, 1926, **20**, 68, 133; **A.**, 141.

Titanous sulphate in the cold reduces salts of gold, palladium, and platinum (and some base metals) to the metallic state and thus effects a separation from iridium; a method for the separation of platinum and rhodium depending upon this reduction is given.[86] The treatment of the iridium–ruthenium–iron alloy (obtained after extraction of a lead button) necessary to isolate the iridium is described in detail.[87]

Except in very small concentrations of the metal, the brownish-red colour produced by hydrogen peroxide with solutions of molybdic acid containing excess of sodium hydroxide can be used, under certain conditions, for the determination of molybdenum. Ammonium salts must first be removed by boiling the solution with sodium hydroxide.[88] A solution of quinquevalent vanadium in phosphoric acid is reduced quantitatively by the addition of potassium iodide to the quadrivalent state, with liberation of the equivalent amount of iodine.[89]

Tellurium is completely precipitated as the element by boiling its solutions in alkali sulphides with sodium sulphite; in the presence of potassium cyanide, separation from gold, copper, and selenium can be effected. Lead, bismuth, and mercury must first be removed by appropriate methods.[90] Solutions of selenious or tellurous acid can be determined in the absence of hydrochloric acid, by titration with permanganate in the presence of disodium phosphate; if the two elements are present together, the tellurium is determined first of all by dichromate.[91]

In the absence of heavy metals, small quantities of bromides, chlorides, cyanides, and thiocyanates may be titrated with mercuric nitrate, sodium nitroprusside being used as indicator and the Tyndall effect being employed to observe the end-point. The method is applied to perchloric acid after reducing it by means of titanous sulphate and oxidising the excess with ammonium persulphate.[92] Comparison has been made of several methods of evaluating perchlorates[93] and full details for conversion into chloride without loss of chlorine by heating with sodium carbonate are

[86] I. Wada and T. Nakazono, *Sci. Papers Inst. Phys. Chem. Res.*, 1923, **1**, 139; **A.**, 1926, 141.

[87] W. R. Schoeller, *Analyst*, 1926, **51**, 392; **A.**, 931.

[88] A. D. Funck, *Z. anal. Chem.*, 1926, **68**, 283; **A.**, 815.

[89] T. Heczko, *ibid.*, p. 461; **A.**, 1926, 1020.

[90] A. Brukl and W. Maxymowicz, *ibid.*, p. 14; **A.**, 1926, 490.

[91] W. T. Schrenk and B. L. Browning, *J. Amer. Chem. Soc.*, 1926, **48**, 2550; **A.**, 1115.

[92] F. König, *Z. anal. Chem.*, 1926, **68**, 385; **A.**, 1017.

[93] D. Dobroserdov, *Ukraine Chem. J.*, 1926, **2**, 1; **A.**, 928.

given.[94] This reduction may also be effective by fusion with sodium nitrate and gradual addition of copper powder.[95]

Small quantities of iodide, bromide, and chloride may be estimated with fair accuracy when present together by releasing the halogens one at a time by increasingly powerful oxidising agents. Those selected are acid ferric sulphate for iodine, cold chromic anhydride for bromine, and permanganic acid for chlorine, the halogens being removed by aspiration after treatment.[96] Iodides may be titrated directly in sulphuric or phosphoric acid solution by permanganate, ethyl acetate being present to extract the iodine liberated, thereby enabling the end-point to be discerned; manganous sulphate must be added if bromides and chlorides are also present.[97]

The exact determination of fluorine is a matter of considerable difficulty and continues to attract attention. The ordinary Berzelius method depending upon the precipitation of calcium fluoride always gives low results and quantities of the order of 0·1% may be missed entirely.

For the small amounts found in rocks, the method of G. Steiger,[98] utilising the bleaching effect of fluorides in acid solution on the yellow colour produced by hydrogen peroxide with titanium sulphate, is well adapted for use. Calibration curves must be constructed for this method and precautions taken as regards the concentration of alkali sulphate, acidity, and temperature.[99] G. Starck [1] showed that with soluble fluorides it is possible to utilise the insolubility of PbFCl for the determination. He found that saturated lead chloride solution effected complete separation from the neutral solution; the precipitate was granular and readily filtered and other salts which did not affect lead exerted no influence. This method has been applied to the determination of fluorine in ores of low or medium fluorine content. The ore is fused with fusion mixture, sulphur is oxidised by sodium peroxide, and the melt is extracted with aqueous sodium carbonate. Some hydrochloric acid is added and the neutralisation is then completed with nitric acid. PbFCl is precipitated by means of lead acetate containing acetic acid. The precipitate is filtered off, washed, and redissolved in nitric acid and the chlorine contained is determined by a suitable

[94] D. Dobroserdov and V. Erdmann, *Ukraine Chem. J.*, 1926, **2**, 15; **A.**, 927.
[95] K. Kürschner and K. Scharrer, *Z. anal. Chem.*, 1926, **68**, 1; **A.**, 490.
[96] P. L. Hibbard, *Ind. Eng. Chem.*, 1926, **18**, 57, 836; **A.**, 260, 928.
[97] F. L. Hahn and H. Wolf, *Chem.-Ztg.*, 1926, **50**, 674; **A.**, 1220.
[98] *J. Amer. Chem. Soc.*, 1908, **30**, 219.
[99] H. E. Merwin, *Amer. J. Sci.*, 1909, [ii], **28**, 119.
[1] *Z. anorg. Chem.*, 1911, **70**, 173; *A.*, 1911, ii, 436.

method. It was found that zinc, sulphates, and phosphates have but little effect on the result.[2]

A method used by A. Greeff [3] depends upon the fact that the addition of ferric chloride to a neutral solution of fluoride produces a white or faintly buff-coloured precipitate of M_3FeF_6. To the neutral solution of the fluoride, salt and a strong solution of potassium thiocyanate are added and the fluid is titrated with ferric chloride solution until a weak yellow colour persists. The end-point is improved by adding sufficient of a mixture of equal parts of alcohol and ether to the aqueous solution and titrating with ferric chloride until the red colour persists in the ether layer.[4]

The insolubility of thorium fluoride, $ThF_4,4H_2O$, in very dilute nitric acid or in acetic acid [5] provides a method by which as little as 0·01% of fluorine may be detected. The process consists in adding a slight excess of thorium nitrate to the solution, just acidified with nitric or acetic acid. The precipitate is ignited directly to thorium oxide. Phosphates must first be separated in the usual way, whereas silicofluorides precipitate their fluorine directly and can be estimated. In this process the acidity is best kept within the limits of $N/5$ to $N/50$ of acetic acid.[6]

The difficulties of fluorine determination in basic slag due to the presence of phosphates and vanadium have been surmounted by fusion, extraction of the melt, neutralisation, and treatment with solid silver sulphate. The last operation and also the filtration of the precipitated phosphate and vanadate are conducted in the dark. The fluorine is then determined colorimetrically at 19° to 26° by the bleaching effect on an acid solution of titanium sulphate containing hydrogen peroxide. Curves are drawn connecting bleaching effect with concentration of fluorine, up to 25 mg. of fluorine.[7] This process is clearly applicable to other phosphates.

Another colorimetric method for fluorine depends on the bleaching of the blue lake produced by zirconium oxychloride with sodium alizarinsulphonate in hydrochloric acid. The fluoride, if not already in solution, is obtained from insoluble fluoride by digestion on a water-bath with 10% zirconium oxychloride solution to which is added an equal volume of concentrated hydrochloric acid and

[2] F. G. Hawley, *Ind. Eng. Chem.*, 1926, **18**, 573; **B.**, 1926, 672.

[3] *Ber.*, 1913, **46**, 2511; *A.*, 1913, ii, 975.

[4] See also W. D. Treadwell and A. Köhl, *Helv. Chim. Acta*, 1925, **8**, 500; *A.*, 1925, ii, 1197.

[5] F. Pisani, *Compt. rend.*, 1916, **162**, 791; *A.*, 1916, ii, 393.

[6] F. A. Gooch and M. Koboyashi, *Amer. J. Sci.*, 1918, [iv], **45**, 370; *A.*, 1918, ii, 177.

[7] R. G. Warren, C. T. Immingham, and H. J. Page, *J. Agric. Sci.*, 1925, **15**, 516.

1 c.c. of a 0·03% solution of sodium alizarinsulphonate. A similar solution is prepared without fluoride and both solutions are diluted to a suitable bulk. Both solutions are then titrated with standard potassium fluoride until the orange tint is the same. The method applies to fluoborates, fluotitanates, fluosilicates, and fluoaluminates.[8] It is shown that optimum precipitation as, *e.g.*, calcium fluoride occurs in the presence of excess of an alkaline-earth ion of concentration 0·027 mol./litre. The addition of a little ferric chloride and some ferrous salt to a fluoride which is to be titrated by using aluminium chloride enables a satisfactory end-point to be obtained in the potentiometric titration.[9]

The azidodithiocarbonate radical, $-S{\cdot}CSN_3$, resembles the halides analytically, Volhard's method affording the best results.[10]

A colorimetric method for the determination of minute quantities of hydroxylamine, based on the reaction with benzoyl chloride followed by addition of ferric chloride, has been described.[11]

Some convenient volumetric process for determining sulphates would be of great advantage generally. It is found [12] that excess barium chloride may be titrated with standard potassium stearate and B.D.H. " universal " indicator, the solution reacting alkaline as soon as all the barium has been precipitated as stearate. Unfortunately, the method breaks down in the presence of 1% or more of neutral salts, which affect the end-point in either direction.[13] In a similar process, the excess barium chloride is estimated by titration with standard potassium chromate until the solution becomes alkaline to methyl-red.[14] Precipitated benzidine sulphate may be titrated with sodium hydroxide; and a modified procedure necessary in the presence of lead is described.[15] For the micro-determination of sulphuric acid, it is recommended to bring about the precipitation with barium chloride in the presence of traces of colloidal celluloid, which cause rapid flocculation of the barium sulphate. The method of preparing the celluloid is described and it is stated that adsorption of barium chloride is negligible with the small quantities used in micro-analysis.[16]

[8] J. H. de Boer and J. Basart, *Z. anorg. Chem.*, 1926, **126**, 213; **A.**, 590.
[9] W. D. Treadwell and A. Köhl, *Helv. Chim. Acta*, 1926, **9**, 470; **A.**, 701.
[10] A. W. Browne and G. B. L. Smith, *J. Amer. Chem. Soc.*, 1925, **47**, 2698; **A.**, 1926, 39.
[11] G. W. Pucher and H. A. Day, *J. Amer. Chem. Soc.*, 1926, **48**, 672; **A.**, 490.
[12] H. Atkinson, *Analyst*, 1925, **50**, 590; **A.**, 1926, 38; *ibid.*, 1926, **51**, 140; **B.**, 358.
[13] *Idem, ibid.*, 1926, **51**, 81; **A.**, 261.
[14] A. A. Briwul, *Z. anorg. Chem.*, 1926, **156**, 210; **A.**, 1221.
[15] Vlastimil and M. Matula, *Chem.-Ztg.*, 1926, **50**, 486; **A.**, 928.
[16] E. Eigenberger, *Z. anal. Chem.*, 1926, **68**, 220; **A.**, 701.

Two methods of procedure for the permanganate titration of hypophosphorous acid and its salts, and the precautions for preventing undesirable reduction of the permanganate, have been investigated.[17]

Water Analysis.

Free chlorine may be detected and determined in water for drinking purposes by means of the red colour developed on treatment with acetic acid and then with dimethyl-*p*-phenylenediamine. The comparison is made with standard iodine solutions treated similarly.[18] The sensitivities of the *o*-tolidine and the starch–iodide test for chlorine have been compared.[19] For the determination of iodides in natural waters, a method depending on oxidation to iodate by means of hypochlorite has been worked out; addition of potassium iodide to the acid solution then results in the liberation of a quantity of iodine six times as great as that originally present as iodide.[20]

The somewhat high values found by titration for the carbonic acid concentration of distilled water are due to improperly neutralised indicators and to the slowness with which the carbon dioxide escapes into the atmosphere; the requisite conditions for this determination are discussed.[21]

The methods for the determination of dissolved oxygen have been critically reviewed;[22] treatment with ferricyanide, hypochlorite, permanganate, carbamide, or azoimide for the purpose of eliminating interfering oxidisable impurities is not considered to be of general value. A new method is advanced using bromine for the oxidation of interfering substances, the excess being removed by salicylic acid; Winkler's method, unmodified, is then applied. Apparatus for this determination has been adapted so that only small quantities of water are required.[23]

Methyl-red is not a suitable indicator for ascertaining the hydrogen-ion concentration of waters approaching neutrality; for distilled water, the sodium salt of methyl-red or of chlorophenol-red is better, but the most accurate indicator is heptamethoxy-

[17] D. Köszegi, *Z. anal. Chem.*, 1926, **68**, 216; **A.**, 702; I. M. Kolthoff, *ibid.*, 1926, **69**, 36; **A.**, 1018.

[18] I. M. Kolthoff, *Chem. Weekblad*, 1926, **23**, 203; **B.**, 517.

[19] A. M. Buswell and C. S. Boruff, *J. Amer. Water Works Assoc.*, 1925, **14**, 384; **B.**, 1926, 174.

[20] H. W. Brubaker, H. S. van Blarcom, and N. H. Walker, *J. Amer. Chem. Soc.*, 1926, **48**, 1502; **B.**, 630.

[21] I. M. Kolthoff, *Biochem. Z.*, 1926, **176**, 101; **A.**, 1116; *Chem. Weekblad*, 1926, **23**, 381; **A.**, 1018.

[22] G. Alsterberg, *Biochem. Z.*, 1926, **170**, 30; **A.**, 591.

[23] C. Risch, *ibid.*, 1925, **161**, 465; **A.**, 1926, 140.

triphenylcarbinol.[24] For such unbuffered solutions, bromothymol-blue should be adjusted to a pure dark green colour by addition of alkali; since, however, this solution is not stable, a neutral solution of *p*-nitrophenol is preferred.[25]

A series of solutions of p_H values ranging from 12·5 to 2 and calibrated by means of the quinhydrone electrode has been prepared in a medium consisting of acetone and water (9 : 1 by volume); the colour changes of a large number of indicators with these solutions and with water are tabulated.[26] Permanent standards prepared from potassium chromate and dichromate are recommended for comparison with nitro- and dinitro-phenols in the determination of hydrogen-ion concentration.[27] The use of methyl-orange or dimethyl-yellow gives slightly high p_H values with the hydrogen phthalate series of solutions, for which bromophenol-blue or methyl-red is better suited; the Sörensen series of citrate solutions are recommended for use with methyl-orange.[28] Standard alkaline buffers produce with some indicators a salt error which in extreme cases may amount to two units as compared with the p_H values of sodium hydroxide solutions.[29]

Gas Analysis.

For the colorimetric determination of free chlorine in air by the use of *o*-tolidine, comparison is made with a series of standards made by mixing dilute solutions of copper sulphate and potassium dichromate.[30] A study of the concentrations of cuprous chloride necessary to obtain maximum absorption of carbon monoxide shows that the ammoniacal solutions are more efficient than acid solutions.[31] In a review of the various methods for the detection and determination of carbon monoxide in small concentrations, it is shown that accurate quantitative results are obtained only by combustion. With practice, however, the time required to produce a coloration with ammonium chloropalladite or with ammoniacal silver nitrate affords a fairly accurate measure of the concentration of the gas in air.[32]

[24] I. M. Kolthoff, *Chem. Weekblad*, 1925, **22**, 590; **A.**, 1926, 139.
[25] H. T. Stern, *J. Biol. Chem.*, 1925, **65**, 677; **A.**, 1926, 38.
[26] F. M. Cray and G. M. Westrip, *Trans. Faraday Soc.*, 1925, **21**, 326; **A.**, 1926, 374.
[27] A. Janke and S. Kropacsy, *Biochem. Z.*, 1926, **174**, 120; **A.**, 927.
[28] I. M. Kolthoff, *Rec. trav. chim.*, 1926, **45**, 433; **A.**, 701.
[29] J. W. McBain, O. E. Dubois, and K. G. Hay, *J. Gen. Physiol.*, 1926, **9**, 451; **A.**, 590.
[30] L. E. Porter, *Ind. Eng. Chem.*, 1926, **18**, 730; **A.**, 927.
[31] L. Moser and F. Hanika, *Z. anal. Chem.*, 1926, **67**, 448; **A.**, 375.
[32] H. Kast and H. Selle, *Gas- u. Wasserfach*, 1926, **69**, 812; **A.**, 1018.

Organic Analysis.

Qualitative.—A large number of qualitative tests for formaldehyde have been critically examined with the view of ascertaining those best suited for the detection of small quantities, particularly in the presence of such substances as acetaldehyde, furfuraldehyde, and carbohydrates. In each case the sensitivity is indicated.[33]

Primary alkyl bromides and iodides are readily converted into the corresponding mercuric alkyl halides, which are well-defined substances suitable for purposes of identification.[34] The monosubstituted acetylenes also may be identified by the formation of characteristic mercury derivatives, $(CR{\equiv}C)_2Hg$.[35]

3 : 5-Dinitrobenzoyl chloride is particularly suitable as a reagent for alcohols; the esters form definite molecular compounds with α-naphthylamine. A number of esters from anthraquinone-β-carboxyl chloride are also described.[36] α-Naphthylcarbimide reacts readily with primary and secondary alcohols, less readily with tertiary, giving urethane derivatives.[37] Examination of the products of reaction of their toluenesulphonates with ammonia, amines, or hydrazine enables a distinction to be made between primary alcohols, secondary alcohols, and phenols.[38]

A review of the colorimetric tests for lactic acid depending upon the formation of acetaldehyde and subsequent reaction with phenols shows that these are, in general, not very trustworthy. Phloroglucinol and *p*-cresol are the most sensitive phenols. Methods for the isolation and identification of the acid in gastric juices are given.[39] The purple colour of the ferric salicylate complex is changed by the addition of minute quantities of substances capable of repressing the ferric ion, and a method of testing for the absence of citrates or tartrates is based on this effect.[40]

The red colour given by quinine on addition of bromine and phenylhydrazine hydrochloride followed by ammonia is not shown by other common alkaloids. It is inhibited by alkalis, morphine, codeine, and excess of reagents.[41] Either benzidine or citric acid

[33] T. Sabalitschka and C. Harnisch, *Pharm. Zentr.*, 1926, **67**, 289, 309, 324, 339, 357, 371, 387; **A.**, 853.

[34] C. S. Marvel, C. G. Gauerke, and E. L. Hill, *J. Amer. Chem. Soc.*, 1925, **47**, 3009; **A.**, 1926, 144.

[35] J. R. Johnson and W. L. McEwen, *ibid.*, 1926, **48**, 469; **A.**, 495.

[36] T. Reichstein, *Helv. Chim. Acta*, 1926, **9**, 799, 803; **A.**, 1225.

[37] V. T. Bickel and H. E. French, *J. Amer. Chem. Soc.*, 1926, **48**, 747; **A.**, 517.

[38] K. Freudenberg and H. Hess, *Annalen*, 1926, **448**, 121; **A.**, 935.

[39] G. Capelli, *Ann. Chim. Appl.*, 1925, **16**, 53; **A.**, 1926, 632.

[40] J. B. Peterson, *Ind. Eng. Chem.*, 1925, **17**, 1146; **A.**, 1926, 84.

[41] G. W. Hargreaves, *J. Amer. Pharm. Assoc.*, 1926, **15**, 100; **A.**, 967.

in sulphuric acid solution gives with morphine and several related alkaloids a series of colour changes which may be extended by dilution and addition of ammonia.[42] 3 : 5-Dinitrobenzoic acid gives well-defined, crystalline precipitates with some of the principal alkaloids and is recommended as a reagent for their recognition; photomicrographs are appended.[43]

The characteristic colorations given with phosphomolybdic acid followed by ammonia constitute a sensitive reaction for distinguishing between *o*-, *m*-, and *p*-dihydroxyphenols.[44]

Colour reactions for phenols are obtained by dusting sodium nitroprusside over the surface of a solution standing over concentrated sulphuric acid and shaking gently until the surface of contact becomes coloured.[45] α-Naphthylcarbimide reacts readily with hot monohydric phenols and with aromatic amines, giving urethanes and carbamides, respectively.[46]

Quantitative.—Modifications of the Kjeldahl method for nitrogen, employing copper powder or an iron–copper couple, have been described which give good results with such compounds as phenylhydrazine, alkaloids, and pyrazolone ring compounds.[47] Other variations of the method are described.[48]

An apparatus is described for the determination of arsenic and of mercury in organic compounds by treatment in a current of hydrogen, the elements being weighed as such.[49] In the absence of halogens, selenium may be determined in an organic compound by the ordinary Carius combustion, whereby selenious acid is formed; this is estimated by titration with silver in the presence of zinc oxide.[50]

In the alkalimetric determination of formaldehyde by means of sodium sulphite, thymolphthalein is a better indicator, particularly for dilute solutions, than phenolphthalein; still better results are afforded by the latter indicator if the solution be saturated with sodium chloride before titration.[51]

[42] L. Ekkert, *Pharm. Zentr.*, 1926, **67**, 498; **A.**, 965.
[43] E. Navarro, *Anal. Fis. Quím.*, 1926, **24**, 283; **A.**, 965.
[44] K. Brauer, *Chem.-Ztg.*, 1926, **50**, 553; **A.**, 1036.
[45] L. Ekkert and L. W. Winkler, *Pharm. Zentr.*, 1926, **67**, 566; **A.**, 1033.
[46] H. E. French and A. F. Wirtel, *J. Amer. Chem. Soc.*, 1926, **48**, 1736; **A.**, 830.
[47] K. Kürschner, *Z. anal. Chem.*, 1926, **68**, 209; **A.**, 702; see also K. Kürschner and K. Scharrer, *ibid.*, p. 1; **A.**, 490.
[48] A. C. Andersen and B. M. Jensen, *ibid.*, 1926, **67**, 427; **A.**, 375; A. Elek and H. Sobotka, *J. Amer. Chem. Soc.*, 1926, **48**, 501; **A.**, 632.
[49] H. ter Meulen, *Rec. trav. chim.*, 1926, **45**, 364, 368; **A.**, 490, 492.
[50] W. E. Bradt and R. E. Lyons, *J. Amer. Chem. Soc.*, 1926, **48**, 2642; **A.**, 1266.
[51] K. Täufel and C. Wagner, *Z. anal. Chem.*, 1926, **68**, 25; **A.**, 535.

A convenient table has been constructed showing the relation between percentage, density, and freezing point of acetic acid for concentrations of 90% and upwards; the disturbing effect of propionic acid is discussed.[52] A rapid thermometric method for evaluating acetic anhydride depends upon the reaction with aniline, toluene being used as a diluent.[53] A gasometric method involving the decomposition of anhydrous oxalic acid in dry pyridine by acetic anhydride into carbon monoxide and dioxide has also been described.[54]

A general method for the determination of the carbonyl group depends upon the conversion of the aldehyde or ketone into the corresponding phenylhydrazone, the excess of phenylhydrazine being determined iodometrically.[55] It is claimed that this method is better than that of Benedikt and Strache (*A.*, 1893, ii, 560), which employs Fehling's solution. The *iso*propylidenedioxy-group may be determined by hydrolysis with hydrochloric acid; the liberated acetone is determined iodometrically.[56]

Dehydration of alcohols may result in the formation of unsaturated hydrocarbons or cyclic hydrocarbons. The former may be estimated in the presence of the latter by the action of perbenzoic acid in chloroform solution.[57] Dihydroxyacetone boiled with phosphomolybdic acid reduces it 180 times as rapidly as does dextrose, thus permitting a colorimetric determination of the dihydroxyacetone in the presence of dextrose.[58]

Conditions for the determination of diguanide gravimetrically as the nickel derivative, $Ni(C_2H_6N_5)_2$, have been worked out together with the extra precautions rendered necessary by the presence of guanylcarbamide.[59]

Arginine in fairly acid solution is precipitated quantitatively by flavianic acid (2 : 4-dinitro-α-naphthol-7-sulphonic acid) even in presence of histidine, and may be determined microchemically by this means.[60] The tryptophan content of proteins is readily and accurately ascertained by means of the reaction with formaldehyde and sulphuric acid.[61] A number of other papers also deal

[52] H. D. Richmond and E. H. England, *Analyst*, 1926, **51**, 283; **B.**, 645.
[53] H. D. Richmond and J. A. Eggleston, *ibid.*, p. 281; **B.**, 645.
[54] E. L. Whitford, *J. Amer. Chem. Soc.*, 1925, **47**, 2939; **A.**, 1926, 189.
[55] E. G. R. Ardagh and J. G. Williams, *ibid.*, p. 2983; *Trans. Roy. Soc. Canada*, 1925, [iii], **19**, III, 73; **A.**, 1926, 189.
[56] A. Grün and R. Limpächer, *Ber.*, 1926, **59**, [*B*], 695; **A.**, 632.
[57] S. Nametkin and L. Brüssoff, *J. pr. Chem.*, 1926, [ii], **112**, 169; **A.**, 420.
[58] W. R. Campbell, *J. Biol. Chem.*, 1926, **67**, 59; **A.**, 443.
[59] C. D. Garby, *Ind. Eng. Chem.*, 1926, **18**, 819; **A.**, 1164.
[60] A. Kossel and W. Staudt, *Z. physiol. Chem.*, 1926, **156**, 270; **A.**, 967.
[61] J. Tillmans and A. Alt, *Biochem. Z.*, 1925, **164**, 135; **A.**, 1926, 189 O. Fürth, *ibid.*, 1926, **169**, 117; **A.**, 633.

with the determination of certain amino-acids.[62] The precipitation of proteins, pure or impure, by means of trichloroacetic acid has been investigated from the quantitative aspect.[63]

Aldehyde sugars are completely oxidised to the corresponding acids in the cold by excess of standard iodine in alkaline solution.[64] 2 : 4-Dibromophenylhydrazine furnishes a means of quantitatively separating galactose from xylose, rhamnose, dextrose, lævulose, maltose, and lactose, but not from arabinose.[65]

Aromatic nitro-compounds may be determined by reduction in the cold with titanous chloride in the presence of sodium citrate. After a short period, the excess of the reducing agent is estimated either potentiometrically by means of iron alum or volumetrically with thiocyanate as indicator.[66] An advantage claimed for this procedure is that chlorination of the nitro-compound does not occur. Nitrobenzene is reduced by titanous chloride in presence of sodium hydroxide; the excess of titanous chloride is oxidised in air, and the resultant aniline estimated by the bromide–bromate method.[67] A gasometric method of estimating primary aromatic amines is based upon diazotisation and decomposition in a nitrometer of the diazo-compound with acid ferrous sulphate solution; the nitric oxide formed is removed and the volume of nitrogen then remaining is found to be equivalent to the amine present.[68] Aniline and similar aromatic amines may be accurately titrated potentiometrically with sodium nitrite solution, an average potential of + 0·58 volt at the end-point being independent of the amine.[69] In the absence of free mineral acid, benzidine is completely precipitated by mercuric chloride as benzidine mercurichloride; conversely, mercury is quantitatively precipitated by excess of benzidine acetate.[70]

The oxidation of quinol by iodine is quantitative only if the hydrogen-ion concentration is less than $10^{-5}N$ at the end-point. Methods for the determination by chemical or potentiometric means

[62] M. T. Hanke, *J. Biol. Chem.*, 1925, **66**, 475, 489; **A.**, 1926, 633; J. M. Looney, *ibid.*, 1926, **69**, 519; **A.**, 1050; S. L. Jodidi, *J. Amer. Chem. Soc.*, 1926, **48**, 751; **A.**, 535; Y. Okuda, *J. Dept. Agric. Kyusha Univ.*, 1925, **1**, 163; **A.**, 1926, 190.

[63] F. B. Seibert, *J. Biol. Chem.*, 1926, **70**, 265; **A.**, 1164.

[64] M. E. Pauchard, *J. Pharm. Chim.*, 1926, **8**, 248; **A.**, 535.

[65] E. Votoček, V. Ettel, and B. Koppova, *Bull. Soc. chim.*, 1926, [iv], **39**, 278; **A.**, 501.

[66] I. M. Kolthoff and C. Robinson, *Rec. trav. chim.*, 1926, **45**, 169; **A.**, 420.

[67] I. M. Kolthoff, *Chem. Weekblad*, 1925, **22**, 558; **A.**, 1926, 84.

[68] P. Grigorjev, *Z. anal. Chem.*, 1926, **69**, 47; **A.**, 1049.

[69] E. Müller and E. Dachselt, *Z. Elektrochem.*, 1925, **31**, 662; **A.**, 1926, 314.

[70] W. Herzog, *Chem.-Ztg.*, 1926, **50**, 642; **A.**, 1050.

are described, as well as the use of dichromate as the oxidising agent.[71]

Physical Methods.

A study of the absorption spectra of a large number of solutions of different dyes has demonstrated that the width, B, of the absorption band is connected with the concentration by the expression $B = Ae^{ad+\gamma}$, where d is the thickness of the solution and A and γ are constants for absorption bands.[72] Absorption-spectra maxima have been listed for the azo-dyes obtained from a number of phenols by coupling with *p*-nitrobenzenediazonium chloride.[73]

Magnesium electrodes are recommended for the production of both arc and spark spectra, since the magnesium lines between 7000 and 3500 Å. are not numerous and do not mask those of other elements.[74] Data are given relating to the transmissive properties of the various types of spectral filters employed for visible, ultra-violet, and infra-red radiation.[75]

Details are given for the spectroscopic detection of extremely minute quantities of mercury in vacuum tubes.[76]

The quantity of ozone present in the atmosphere has been determined by measuring the intensity of a number of Fraunhofer transmission lines in the region of the ultra-violet absorption band of ozone at 3000 to 3300 Å.[77] Most inorganic substances exhibit no fluorescence or phosphorescence when examined in the ultra-violet light (from a mercury arc) of wave-lengths 4400 to 2800 Å., but many salts do fluoresce. This test may be used to indicate certain impurities.[78]

The radio-micrometer has been used to measure the iodine content of starch–iodide.[79]

Small quantities of water may be determined in methyl alcohol, otherwise pure, by measuring the critical solution temperature of the sample with hexane.[80]

A simple X-ray spectrograph of the rotating-crystal type is described,[81] and details of a high-vacuum X-ray spectrometer with

[71] I. M. Kolthoff, *Rec. trav. chim.*, 1926, **45**, 745; **A.**, 1266.
[72] J. Šebor, *Chem. Listy*, 1926, **20**, 55, 174; **A.**, 590.
[73] H. Wales and S. Palkin, *J. Amer. Chem. Soc.*, 1926, **48**, 810; **A.**, 515.
[74] E. Dureuil, *Compt. rend.*, 1926, **182**, 1020; **A.**, 593.
[75] K. S. Gibson, *J. Opt. Soc. Amer.*, 1926, **13**, 267; **A.**, 1117.
[76] J. J. Manley, *Proc. Physical Soc.*, 1926, **38**, 127; **A.**, 376.
[77] G. M. B. Dobson and D. N. Harrison, *Proc. Physical Soc.*, 1925, **38**, 74; **A.**, 1926, 140.
[78] R. Robl, *Z. angew. Chem.*, 1926, **39**, 608; **A.**, 701.
[79] J. Field and L. G. M. Baas-Becking, *J. Gen. Physiol.*, 1926, **9**, 445; **A.**, 590.
[80] M. M. Rising and J. S. Hicks, *J. Amer. Chem. Soc.*, 1926, **48**, 1929; **A.**, 967.
[81] J. T. Norton, *J. Opt. Soc. Amer.*, 1926, **13**, 231; **A.**, 1020.

rotatory plate-holder and suitable crystal gratings for particular ranges of wave-lengths are given.[82]

Electrochemical Methods.

Electrolytic.—Polarisation curves of solutions of metals containing traces of more noble metals from the electrochemical point of view, obtained with the aid of the dropping mercury cathode, show a number of undulations the positions and dimensions of which are characteristic of the metallic impurities present. Various applications of this process are described, which is sensitive to about 10^{-7} g.-equivalent of metal per litre.[83]

Copper free from cadmium may be deposited at 1 amp. and 4 volts by electrolysis with a rotating anode of a nitrate solution containing nitric, tartaric, and hydrofluoric acids,[84] whilst complete separation from bismuth is obtained by electrolysis at 60° of a solution of the metals containing phosphoric acid.[85]

Conditions have been worked out for the electro-deposition of antimony from hydrochloric acid solution containing hydrazine sulphate.[86] Tellurium also may be rapidly determined by electrolysis in a malonic acid solution containing ammonium sulphate and tartrate.[87]

Potentiometric.—The reduction of compounds of the platinum metals to the metals by means of titanous chloride in acid solution has been followed potentiometrically; very sharp end-points are obtained with palladium and platinum.[88] Mercuric salts are reduced to metallic mercury by titanous chloride in hot acetic acid solution, containing ammonium chloride and also a bismuth salt as carrier. The method may be applied in the presence of arsenious, antimonious, stannic, lead, cadmium, and bismuth salts and of small quantities of iron salts.[89] Iron may be determined, following reduction with stannous chloride, in hydrochloric acid solution, by titration at 50° with standard potassium bromate in the presence of cobalt chloride. The amount of bromate used in the oxidation is ascertained from the positions of the two turning points (stannous to stannic and ferrous to ferric) on the titration curve.[90] A similar

[82] M. Siegbahn and R. Thoræus, *J. Opt. Soc. Amer.*, 1926, **13**, 235; **A.**, 1020.
[83] J. Heyrovský, *Chem. Listy*, 1926, **20**, 122; **A.**, 590.
[84] A. Jílek and J. Lukas, *ibid.*, p. 18; **A.**, 262.
[85] W. Moldenhauer, *Z. angew. Chem.*, 1926, **39**, 454; **A.**, 592.
[86] A. Schleicher with L. Toussaint and P. H. Troquay, *Z. anal. Chem.*, 1926, **69**, 39; **A.**, 1020.
[87] J. Lukas and A. Jílek, *Chem. Listy*, 1926, **20**, 396; **A.**, 1018.
[88] F. Müller, *Z. anal. Chem.*, 1926, **69**, 167; **A.**, 1222.
[89] E. Zintl and G. Rienäcker, *Z. anorg. Chem.*, 1926, **155**, 84; **A.**, 929.
[90] O. Collenberg and K. Sandved, *ibid.*, 1925, **149**, 191; **A.**, 1926, 140.

method serves for the determination of gold, any aurous chloride present being first oxidised by addition of chlorine water; the solution is then titrated against standard ferrous sulphate.[91]

If the potentiometric titrations of cerous and cupric ions with potassium ferrocyanide and of barium, lead, and mercurous ions with potassium chromate are carried out at 70° in a 30% ethyl-alcoholic medium, errors due to solubility of the precipitates and to adsorption of ions thereon are eliminated and the potential at the end-point is rendered much sharper and steeper.[92]

By suitable adjustment of conditions, it has been found possible to effect progressive separation of iodide, bromide, and chloride (as the silver salts) from ammoniacal solution.[93] Important investigations and improvements in the potentiometric titration of halides have also been made and Clark's method lends itself to the accurate determination of the three halides in mixtures.[94]

A platinum electrode, coated electrolytically with gold, is suitable for the titration of oxidising acids. The results obtained with chromic, iodic, and periodic acids are described, the *E.M.F.* being a linear function of the p_H value of the acid, but varying with different acids.[95] In the determination of phosphates by titration with a uranyl solution in presence of acetic acid, the addition of quinol or potassium ferrocyanide affords a sharper end-point. Alternatively, using a mercury electrode, titration may be carried out at 70° after addition of a known amount of mercurous sulphate, the fall in voltage at the end-point being very sharp.[96]

Aromatic nitroso- and nitro-compounds may be titrated directly at 50—80° with titanous chloride, alcohol being used as solvent if necessary. The break in the curve is much more pronounced in presence of Rochelle salt.[97]

Attention is directed to the advantages of, and methods are given for using, the quinhydrone electrode in the measurement of hydrogen-ion concentration, by a number of authors.[98]

The potential of a platinum electrode against a solution con-

[91] E. Müller and F. Weisbrod, *Z. anorg. Chem.*, 1926, **156**, 17; **A.**, 1117.

[92] J. A. Athanasiu, *Compt. rend.*, 1926, **182**, 519; **A.**, 376; *J. Chim. phys.*, 1926, **23**, 501; **A.**, 929.

[93] H. T. S. Britton, *Analyst*, 1925, **50**, 601; **A.**, 1926, 39.

[94] W. Clark, *J.*, 1926, 749; **A.**, 590; E. Lange and E. Schwartz, *Z. Elektrochem.*, 1926, **32**, 240; **A.**, 701.

[95] L. Malaprade, *Bull. Soc. chim.*, 1926, [iv], **39**, 325; **A.**, 490.

[96] S. Bodforss, *Svensk Kem. Tidskr.*, 1925, **37**, 296; **A.**, 1926, 1018.

[97] E. Dachselt, *Z. anal. Chem.*, 1926, **68**, 404; **A.**, 1049.

[98] W. Ackermann, *Collegium*, 1926—1927, 208; **A.**, 813; A. Hock, *Z. angew. Chem.*, 1926, **39**, 647; **A.**, 701; C. W. G. Hetterschij and J. Hudig, *Chem. Weekblad*, 1926, **23**, 2; **A.**, 139; J. B. O'Sullivan, *Trans. Faraday Soc.*, 1925, **21**, 319; *A.*, 1925, ii, 822; L. Smolik, *Biochem. Z.*, 1926, **172**, 171; **A.**, 927.

taining both ferrous and ferric ions is a function of the ratio of the two ions present under limiting conditions of concentration and acidity. If E_0 is the potential of the electrode against the acid alone and E that of the solution when iron salts are present, then at 18° we have $E = E_0 + 0{\cdot}0577 \log \{[Fe^{\cdots}]/[Fe^{\cdot\cdot}]\}$. Hence the total iron or the ferrous iron in a solution having been determined, measurement of the potential under standard conditions enables the proportion of each of the iron ions to be ascertained.[99] A new method for the conductometric analysis of weak acids and bases has been described,[1] and also a method, applicable to iodometry, in which a *P.D.*, between two platinum electrodes immersed in the well-stirred iodine solution, of the same order as the polarisation *E.M.F.* is maintained.[2]

Simple comparison electrodes for the titration of reducing substances such as arsenious oxide and ferrous and vanadyl salts with permanganate have been developed and details of the electrodes are furnished.[3]

J. J. Fox.
B. A. Ellis.

[99] P. Hirsch and R. Rüter, *Z. anal. Chem.*, 1926, **68**, 328; **A.**, 930.
[1] P. Hirsch, *ibid.*, p. 160; **A.**, 700.
[2] C. W. Foulk and A. T. Bawden, *J. Amer. Chem. Soc.*, 1926, **48**, 2045; **A.**, 927.
[3] R. Lang, *Z. Elektrochem.*, 1926, **32**, 454; **A.**, 1116.

BIOCHEMISTRY.

The material in this Report is arranged in the same manner as that adopted in the past two years: soil, plant, and animal biochemistry. In one respect, however, an alteration has been made. Work on the physical and inorganic chemistry of the soil has been omitted, in so far as questions of what may be termed pure soil chemistry are concerned. These have been left for discussion in the Report by one of us on Soils and Fertilisers in the Annual Reports on Applied Chemistry. The soil problems dealt with in this Report are those in which biochemical processes in the soil itself, or the relation of soil conditions to plant growth, are involved.

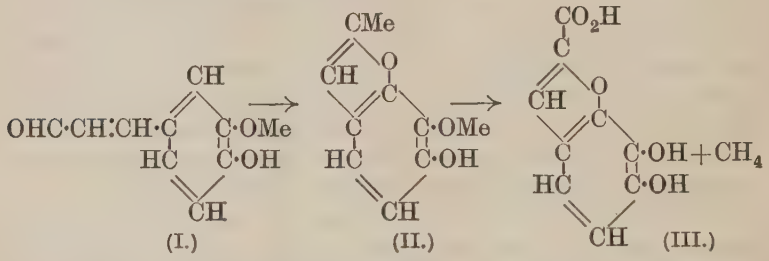
There is no advance of outstanding importance to record, at least as far as soil and plant biochemistry are concerned. Since the war, great advances have been made in our knowledge of the chemistry of the soil, and we appear now to have reached the stage where the new points of view are being consolidated and matters of detail are being cleared up, in preparation for further advances. With regard to plant chemistry, we are still groping in the dark without any very clear indication of the direction in which fruitful advances in knowledge are to be found.

The Humic Matter of the Soil.

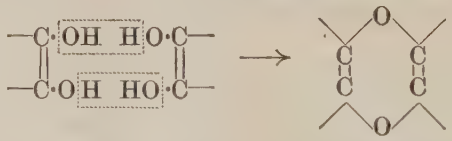
In the Reports for 1924 and 1925,[1] the lignin hypothesis of the origin of humic matter, the detailed development of which is due to F. Fischer[2] and his co-workers, was discussed. This hypothesis continues to gain ground. One type of evidence on which this hypothesis rests is that depending upon the analysis of plant material in various stages of humification. Further evidence of this type has been advanced during the past year by W. Grosskopf[3] and by S. Odén and S. Lindberg.[4] The former investigator analysed successive layers of the humic soil in a pine wood. He found a marked relationship between the loss of lignin and the formation of humic matter. The latter was determined by making use of the solvent action of acetyl bromide, which is stated to dissolve completely all undecomposed plant materials. Odén and Lindberg have similarly analysed a number of peats of varying age. They found that cellulose gradually disappears and that the sum of

[1] *Ann. Reports*, 1924, **21**, 172; 1925, **22**, 206.
[2] See also F. Fischer, *Z. Deuts. Geol. Ges.*, 1925, **A**, **77**, 534; **B.**, 1926, 393.
[3] *Brennstoff-Chem.*, 1926, **7**, 293; **B.**, 939.
[4] *Ibid.*, p. 165; **B.**, 568.

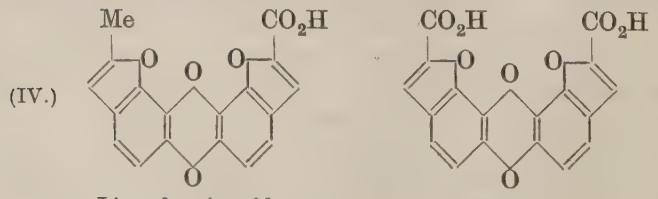
lignin plus humic substances remains more or less constant: as the lignin content falls, humic matter takes its place. From considerations based on P. Klason's views on the constitution of lignin and Eller's [5] views on the chemical nature of the process of humus formation, they develop a hypothesis for the structural relationship of humic acid to lignin. It is supposed that the coniferyl paraldehyde unit of lignin is converted into a conjugated furan derivative by internal condensation thus:



There is some evidence for the presence of furan nuclei in lignin and humic acid. By simultaneous oxidation and reduction of a substance of formula (II), there could be produced the acid (III), containing two phenolic hydroxyl groups in the ortho-position. In an oxidising medium, *o*-dihydroxyphenols of this type readily undergo condensation into a quinonoid substance thus:



The production of a ring of this type is thought to be characteristic of the humification process, which involves the production of strongly coloured products from colourless ones. Odén and Lindberg suggest structural formulæ for humic and ligno-humic acids involving the combination of units of structure (I), (II), and (III). Thus they formulate a ligno-humic acid built up from (II) and (III) and a humic acid built up from two units of formula (III) thus:



Ligno-humic acid. Humic acid.

[5] See *Ann. Report*, 1923, **20**, 209.

Formula (IV) corresponds to an equivalent weight of 322, whilst (V) has an equivalent weight of 352 or 176 according as it behaves as a mono- or a di-basic acid. Odén's earlier determination of the equivalent weight of natural humic acid from peat gave the value 330—345, whilst the value calculated by Hissink from the exchangeable base content of "saturated" humic soils is 176.

These speculations are interesting in that they combine the views of Eller and Fischer, but the present position of the subject does not warrant their being regarded as anything more than speculations.

H. Strache and A. Brandl [6] have determined the carbonyl content of lignin, humic acid, and coal by treatment with phenylhydrazine and determination of the excess of the latter with Fehling's solution. Lignin contained only 0·2%, whilst humic acid from lignite contained 3·2%. The subsequent conversion of lignite into coal involved a fall in the carbonyl content, anthracite containing only 1%. It will be noticed that there are no carbonyl groups in the formulæ proposed by Odén.

S. A. Waksman [7] has published a series of papers dealing with the origin and nature of the humic matter of the soil. The first of these papers consists of a comprehensive review of the literature of the subject. The lack of satisfactory methods of characterising humic matter is emphasised, and it is pointed out that many of the products referred to loosely as humus, humic acid, etc., are undoubtedly not homogeneous; many of the conflicting statements in the literature are due to this fact. In another paper of the series, it is shown that of the various constituents of straw the lignins are the most resistant to the action of fungi and bacteria. Thus they tend to accumulate in the soil, and in Waksman's view they constitute a considerable part of the soil humic matter. If lignins are removed from straw or lucerne meal, the rate of decomposition of the material is hastened and the amount of residual matter is greatly reduced. It was found that when lignin was introduced into the soil it could be recovered almost quantitatively, after incubation, as "humus." As pointed out in last year's Report,[8] the nitrogen content of the humic matter of the soil is not explained by current hypotheses as to the origin of the latter. In that Report attention was directed to Waksman's views on this subject, which are still further developed in the papers now under notice, and to the work of Hobson on the state of the nitrogen in humic acid.

The possibility still exists that the humic matter of soil may be of

[6] *Brennstoff-Chem.*, 1926, **7**, 341.

[7] S. A. Waksman, *Soil Sci.*, 1926, **22**, 123, 323; **B.**, 1926, 892, 990; S. A. Waksman and F. G. Tenney, *ibid.*, p. 395; S. A. Waksman, *ibid.*, p. 421.

[8] *Ann. Report*, 1925, **22**, 208.

a two-fold character. The work of A. C. Thaysen, W. E. Bakes, and H. J. Bunker [9] supports this view. These workers found that the humic matter which constituted a high proportion of an ancient Egyptian linen cloth yielded a chlorine derivative very similar to that obtained from Eller's artificial humic acid. The humic compounds from peat, however, gave on chlorination a mixture of substances partly soluble in ether. The ether-soluble fraction was similar to the chlorine derivative obtained from lignin humic acid, whilst the ether-insoluble fraction resembled the chlorine derivative of the artificial humic acid obtainable from sugar or cellulose.

J. Marcusson,[10] who has hitherto been a firm supporter of the cellulose hypothesis of the origin of humic matter and coal, now believes that both lignin and cellulose are concerned in the process. C. G. Schwalbe and R. Schepp,[11] however, still favour the cellulose hypothesis. They describe the production of humic products and of " coal-like " substances by the action of oxalic acid and magnesium chloride on cellulose, sugars, and wood; sugars are regarded as an intermediate phase in the process. Bergius's results on the artificial production of coal from cellulose and lignin have been criticised by H. Tropsch and A. von Philippovich [12] on the grounds that Bergius neglected to consider the appreciable formation of water-soluble products in his experiments. Further progress in this field of work is hindered by the scanty knowledge of the chemical nature of lignin. A considerable amount of work is, however, now being carried out on this subject. Two valuable monographs on lignin by W. Fuchs [13] and by Kürschner [14] have recently appeared (see also p. 230).

Carbon and Nitrogen Transformations in the Soil.

It is generally recognised that the application of lime or chalk to the soil hastens the decomposition of organic matter, although the view that the action of lime in this respect is greater than that of chalk was shown to be untenable by J. W. White and F. J. Holben [15] on re-examination of the data from the plots of the continuous manurial experiment in Pennsylvania. A further examination of these data shows that on soil regularly carrying crops in rotation the effect of treatment with lime is actually to

[9] *Biochem. J.*, 1926, **20**, 210.
[10] *Z. angew. Chem.*, 1926, **39**, 898; **B.**, 809.
[11] *Ber.*, 1925, **58**, 2500; **B.**, 1926, 145.
[12] *Abhandl. Kennt. Kohle*, 1925, **7**, 84; **B.**, 1926, 858.
[13] " Die Chemie des Lignins " (Berlin), J. Springer, 1926.
[14] " Zur Chemie der Lignin Körper " (Stuttgart), F. Enke, 1925. 116 pp.
[15] *Soil Sci.*, 1925, **20**, 313; **B.**, 1926, 25. See also *Ann. Rep. Appl. Chem.*, 1924, **9**, 438.

cause an increase in the organic matter content of the soil. This is due to the fact that the use of lime, by liberating more plant nutrients from the dung which is added at the same time, gives rise to much larger crops and thus to much larger crop residues (stubble, etc.). The organic matter left in the soil by the decomposition of these residues more than counterbalances the increased loss in organic matter of the added dung caused by the action of the lime.

M. Bach [16] has studied the rate of oxidation of the carbon of farmyard manure which has been added to the soil. As an average of the results obtained with various types of soil, he found that 75% of the added carbon disappeared from the soil in the first year. The loss of pentosans was even more rapid than this, but the loss of lignin was much slower.

On the addition of carbohydrate material to the soil, the production of carbon dioxide as a result of the action of micro-organisms rises to a maximum and then falls. D. V. Bal [17] has made a study of this action in the case of *Bacillus prodigiosus*. He found that the fall in carbon dioxide production occurred despite the fact that there was still present a residue of undecomposed sugar and of sufficient of the other nutrient materials required by the organism. Nevertheless, the addition of a further supply of sugar caused carbon dioxide production again to rise and this effect could be obtained repeatedly by further additions of sugar. This curious result may be in some way connected with the production of toxic by-products by the organism, but further work is needed to establish this.

B. M. Bristol-Roach,[18] in an investigation of the relation of certain soil algæ to various carbohydrates and related compounds, has demonstrated the ability of soil algæ to grow in the dark if a suitable supply of organic food is provided. These algæ are thus able to function either auto-trophically as green plants in the light or hetero-trophically, in the same manner as fungi and most bacteria, in the dark. Their auto-trophic activity can be of little significance in most soils, since it could only occur at the surface (although this effect is of considerable importance in the gaseous exchanges of water-logged soils in the tropics), but the possession of the power of living saprophytically in the interior of the soil renders soil algæ a factor which must be taken into consideration in studying the biochemical changes of the soil.

S. A. Waksman and C. E. Skinner [19] have studied the micro-

[16] *Landw. Vers.-Stat.*, 1926, **104**, 245; **B.**, 640.
[17] *Ann. Appl. Biol.*, 1926, **13**, 231.
[18] *Ann. Bot.*, 1926, **40**, 149.
[19] *J. Bact.*, 1926, **12**, 57.

organisms concerned in the decomposition of celluloses in the soil. They conclude that under anaërobic conditions and in humid soils the fungi are largely concerned in the process, but that in arid and alkaline soils the aërobic bacteria play an important part. Under anaërobic conditions, bacteria are the only organisms concerned. This is true, not only of soils, but probably also of the decomposition of celluloses in all natural processes. Although some *actinomycetes* are capable of decomposing cellulose, they do not seem to play any direct part in this process in the soil; their action is largely limited to the secondary products. As already shown by earlier work by Waksman [20] and by other investigators, the extent of the decomposition of cellulose is dependent on the supply of available nitrogen compounds, but this decomposition goes on to a greater extent in anaërobic than in aërobic conditions for a given supply of available nitrogen, since under anaërobic conditions a much smaller amount of energy is liberated and utilised by the organisms. Further results on the relation between available nitrogen and cellulose decomposition are reported by J. A. Anderson [21]; the maximum decomposition of cellulose was found to occur when the proportion of nitrogen to cellulose equalled or exceeded 1 : 35. Nitrification is not prevented by the presence of cellulose, but the nitrate produced is utilised by the organisms as soon as it is formed. Ammonia can be used by the organisms directly.

The effect of the relation between available nitrogen and fermentable carbohydrate material on the presence of nitrates in the soil and their supply to the growing plant, as well as the bearing of this factor on the carbon : nitrogen ratio of the soil, has been discussed in these Reports for 1923 and 1925,[22] and subsequent work has added little to our knowledge of the position as there set forth. T. L. Lyon,[23] in a paper read at the symposium on soil bacteriology—nitrification studies—held by the American Society of Agronomy at Chicago in November, 1925, has given a useful summary of this question. C. Barthel and N. Bengtsson [24] have shown how the same factor operates in the breakdown of roots and stubble in the soil; thus oat-straw contains enough nitrogen to supply the needs of the bacteria responsible for its decomposition, so that it rots more quickly than pure cellulose in sandy soils of low nitrogen content.

Similarly, R. P. Thomas and H. J. Harper [25] have shown that

[20] *Ann. Report*, 1925, **22**, 207. [21] *Soil Sci.*, 1926, **21**, 115; **B.**, 457.

[22] *Ann. Reports*, 1923, **20**, 213; 1925, **22**, 207.

[23] *J. Amer. Soc. Agron.*, 1926, **18**, 834. See also B. D. Wilson and J. K. Wilson, *Cornell Univ. Agr. Expt. Sta. Memoir*, 95, 1925.

[24] Mitt. 300 der Landw. Zentralversuchanst. (Sweden), 1926; *Bakt. Abhandl.*, **40**, 1; **B.**, 640.

[25] *Soil Sci.*, 1926, **21**, 393; **B.**, 640.

straw can be ploughed in after the second cut of a clover or legume ley without any harmful effect on the succeeding crop; the leguminous residues supply sufficient nitrogen for the decomposition of the carbohydrates of the straw. R. C. Collison and R. J. Conn [26] claim to have shown that the harmful effect of incorporating straw in the soil on the subsequent crop is due to two factors; in addition to the effect in reducing available nitrate, it is claimed that a toxic decomposition product is formed from the straw.

No satisfactory explanation has yet been advanced for the considerable losses of free nitrogen that occur in the manure heap, in sewage, and in soil receiving heavy dressings of dung. M. Lemoigne and P. L. Dopter [27] have isolated various bacteria from soil and dung which are capable of bringing about losses of nitrogen in pure cultures. This loss occurs after their first rapid growth is over.

Other papers dealing with nitrification were read at the above-mentioned symposium by W. A. Albrecht, A. L. Whiting, and H. J. Harper and B. Boatman.[28] Albrecht showed how all normal cultivation operations have an augmenting effect on nitrate production in the soil but excessive cultivation or mulching with straw may cause a decrease. A. L. Whiting has made a study of the factors controlling the rate of nitrification of organic materials. This rate is greatest for water-soluble substances and for readily hydrolysable compounds. Fresh green plant material produces nitrate more quickly than after drying. He gives a useful reference list of more than 200 organic materials which have been classified according to their rate of nitrification. Harper and Boatman show that the nitrification of sulphate of ammonia is more rapid when it is applied in small than in large amounts. H. J. Harper [29] has also examined a large number of soils with regard to their ammonia content in relation to their reaction and their content of total nitrogen and nitrates. He could find no correlation between these factors.

Sulphur and Soil Fertility.

Attention has been directed in recent Reports [30] to the effect of sulphur oxidation on soil reaction and to the possible limitation of fertility in some soils by deficiency of sulphur. R. H. Simon and

[26] *New York Agric. Exp. Stat.*, 1925, Tech. Bull. 114, 35 pp.; **B.**, 1926, 416. See also H. H. Hill, *J. Agric. Res.*, 1926, **33**, 77; **B.**, 840.

[27] *Compt. rend.*, 1926, **183**, 160; **A.**, 979.

[28] W. A. Albrecht, *J. Amer. Soc. Agron.*, 1926, **18**, 841; A. L. Whiting, *ibid.*, p. 854; H. J. Harper and B. Boatman, *ibid.*, p. 876.

[29] *J. Agric. Res.*, 1925, **31**, 549; **B.**, 1926, 335.

[30] *Ann. Reports*, 1922, **19**, 209, 213; 1923, **20**, 214; *Ann. Reports Appl. Chem.*, 1922, **7**, 375; 1923, **8**, 422.

C. J. Schollenberger [31] and R. E. Stephenson [32] have shown that in the soil the rate of oxidation of sulphur depends in a marked degree on its fineness of division. A. Leduc [33] has reviewed the results of various experiments indicating the influence of lack of sulphur on soil productiveness. From the investigations of J. M. Fife,[34] it appears that the benefits obtained by the addition of sulphur to a soil very deficient in this element may be due, not only to the direct influence of the supply of sulphur to the growing plant, but also to a beneficial effect on the micro-organisms concerned in ammonification and nitrification. When sulphur was added to such a soil containing an ample supply of all other nutrients except nitrogen, which was added in the form of dried blood, although there was no rise in the numbers of bacteria developing on nutrient agar, considerable increases in the production of ammonia and nitrates were observed. W. W. Johnston [35] has shown that, on a semi-arid soil in Oregon which had been found to give crop increases when treated with sulphur, the effect of cropping was to decrease the sulphate content, but that in humid soils cropping had the reverse effect. Thus the benefit or otherwise of sulphur additions may depend, not only on the sulphur content of the soil, but also on whether crop growth can stimulate sulphate formation enough to supply the needs of the plant. It can on humid but not on semi-arid soils. J. R. Neller [36] has found that the addition of sulphur or gypsum to soil under greenhouse conditions caused an increase in yield and in the percentage of nitrogen in lucerne and clover. For the liberation of potash in an available form in the soil, sulphur was found to be superior to gypsum by O. M. Shedd.[37] The addition of chalk favoured sulphur oxidation, but hindered liberation of potash.

Plant Nutrition.

Nitrogen Supply.—W. H. Appleton and H. B. Helms [38] have shown that the rate of absorption of sodium nitrate by oats and cotton when applied at different stages of growth is the more rapid the later the nitrate is applied. In both cases, there was a close correlation between the rate of growth and the rate of nitrogen uptake. The effect of the amount of nitrogen supplied, on the growth of the sunflower, has been studied by A. Rippel and O. Ludwig; [39] for smaller rates of nitrogen supply, the actual rate of

[31] *Soil Sci.*, 1925, **20**, 443; **B.**, 1926, 208.
[32] *Ibid.*, 1926, **21**, 489; **B.**, 762. [33] *Scientific Agric.*, 1926, **6**, 218.
[34] *Soil Sci.*, 1926, **21**, 245; **B.**, 600. [35] *Ibid.*, p. 233; **B.**, 457.
[36] *Ind. Eng. Chem.*, 1926, **18**, 72; **B.**, 208.
[37] *Soil Sci.*, 1926, **22**, 335.
[38] *J. Amer. Soc. Agron.*, 1925, **17**, 596; **A.**, 1926, 871.
[39] *Biochem. Z.*, 1926, **177**, 318; **A.**, 1280.

growth is less, but in the first half of the growth curve the relative production of dry matter and the relative absorption of nitrogen are greater with the smaller dressing. The same authors [40] have attempted to correlate the uptake of nitrogen with that of bases for broad beans and oats grown in sand with or without the addition of combined nitrogen. The excess of nitrogen in the plants above that which could have been absorbed in the form of nitrates combined with the bases present in the plant (allowance being made for the bases combined as phosphates and sulphates) is expressed as a percentage excess of nitrogen. As would be expected, this figure is much higher with broad beans when combined nitrogen is withheld. In the case of oats, the excess is still greater when nitrogen is given, whereas nitrogen-starved oats show a large excess of bases. T. W. Turner [41] has demonstrated the contrast between the response of barley and maize, compared with that of flax, to variations in the nitrogen supply. The former two crops show a large increase in the top : root ratio with increasing dressings of nitrate, which is due to a stimulation of the growth of tops, not to a depression of root formation. In the case of flax this effect is not very marked. Beyond a certain low level of nitrogenous dressing, further increases in nitrogen supply produce no appreciable change in the ratio of tops to roots.

No conclusive evidence is available regarding the benefit or otherwise of growing leguminous crops in association with non-legumes. J. H. Stallings [42] has demonstrated that wheat plants grown with soy-beans benefited, apparently by obtaining soluble nitrogen compounds, from the latter. It is possible that this nitrogen was obtained in the form of ammonia, which is the only form of soluble nitrogen that could be found in the growing soy-bean plants.

Phosphate Supply.—It is known that the soil factors governing the supply of phosphate to the growing plant are markedly different from those concerned with the supply of most other nutrients. Much attention is being directed to this question at the present time. M. von Wrangell [43] and her co-workers have published a series of lengthy papers on this subject during the past year. She distinguishes three factors for the supply of phosphate from the soil : (1) the phosphate concentration of the soil solution; (2) the rate at which this concentration is restored after disturbance of the equilibrium between the soil and the soil solution; (3) the total

[40] *Ber. Deut. bot. Ges.*, 1925, **43**, 537; **A.**, 1926, 439.

[41] *Soil Sci.*, 1926, **21**, 303; **B.**, 601.

[42] *Ibid.*, p. 253; **B.**, 601.

[43] M. von Wrangell, *Landw. Jahrb.*, 1926, **63**, 627; M. von Wrangell and E. Koch., *ibid.*, p. 677; M. von Wrangell and W. Haase, *ibid.*, p. 707; M. von Wrangell and L. Meyer, *ibid.*, p. 739; **B.**, 841, 842.

reserve of soluble phosphate in the soil. The phosphate concentration of the soil solution, obtained by the hydraulic press method, is regarded as being particularly important because one is dealing, not only with an easily soluble material, but also with substances of low solubility the concentration of which depends to a large extent on the presence or absence of other ions. The phosphate concentration in the soil solution varies between very wide limits for different soils. Raw subsoil and poor peat soils show values as low as 0·02 mg. P_2O_5 per litre, whilst humic sandy soils and rich garden soils may give values as high as 2 mg. or more per litre. The average value for most soils is from 0·1 to 0·2 mg. per litre. In any given soil, the phosphate concentration of the soil solution is relatively constant and varies little during the year, but according to Wrangell's results it is a function of the moisture content of the soil, increasing with the latter. This is explained by assuming that with increased water content there is an alteration in the structure of the soil particles which renders the phosphates more soluble.

It is considered that the characteristic phosphate concentration of any given soil is determined more by the absorptive power of that soil than by any variation in the chemical nature of the phosphate reserves or of the phosphates added in the form of manure. In support of this view, it is shown that the solubility of the phosphates of calcium, aluminium, and iron in water is much higher than that represented by the phosphate concentration found in soil solutions and is reduced to figures more comparable with the latter only by the presence of lime.

The rate at which the phosphate concentration of the soil solution is restored after reduction of the latter was studied by Wrangell by expressing the soil solution, then remoistening and again expressing the soil solution after varying intervals. Some soils show a rapid rate of readjustment, whilst in others the rate is very slow. This rate is determined by the amount of reserve phosphate in the soil and also by the absorptive power of the latter; soils of low absorptive power give a much more rapid readjustment than do strongly absorptive soils.

The total reserves of relatively soluble phosphate in the soil are regarded as the most important factor in the phosphate nutrition of crops. These reserves are determined by Wrangell by repeated extractions of small quantities of soil with large volumes of water and extrapolation of the curve showing the rate of falling off of phosphate concentration in the successive extracts. The results showed a good correlation with determinations of "available" phosphate by Neubauer's seedling method.

In explanation of the claimed superiority of the determination

of total reserves of phosphate over that of the phosphate concentration of the soil solution as a measure of the amount of available phosphate in the soil, it is suggested that the phosphate concentration of the liquid close to the surface of the soil particles is higher than that in the bulk of the liquid; the root hairs of the plant may therefore be in a position to absorb phosphate from concentrations higher than those indicated by analyses of the soil solution. It is supposed that only in extreme cases can the phosphate concentration fall so low (less than 0·05 mg. per litre) that it becomes a limiting factor in plant growth.

Investigations of a similar type have been carried out in the United States by F. W. Parker and J. W. Tidmore,[44] whose results regarding the characteristic phosphate concentration in the soil solution of different soils are similar to those of Wrangell. They also found that the phosphate concentration of the soil solution and of soil extracts from the untreated soil and from the soil after treatment with superphosphate or basic slag was increased by the addition of lime. No marked effect was observed in the case of soils treated with rock phosphate, whilst after the addition of steamed bone flour lime caused a reduction in phosphate concentration. Parker and Tidmore put forward similar views to those of Wrangell with regard to the probable existence of a higher concentration of phosphate in the immediate neighbourhood of the soil particles than in the bulk of the soil solution, which they explain by the application of the Donnan theory. They differ, however, from Wrangell in regard to the limit of phosphate concentration below which the plant is supposed to suffer from deficient phosphate supply. Wrangell carried out water-culture experiments in which the concentration of the medium was maintained by constant circulation. Her results appear to show that plants were able to utilise phosphate from solutions at least as dilute as 0·1 mg. P_2O_5 per litre; she places the limit provisionally at 0·03 mg. per litre. Parker and Tidmore, on the other hand, base their views on the results of D. R. Hoagland and J. C. Martin,[45] who found that barley in water culture grew satisfactorily with a concentration of phosphate of 1·1 mg. per litre but suffered when the value fell to 0·7 mg. per litre. One respect in which these views appear to be inadequate is in regard to the marked difference in the ability of different plants to utilise insoluble phosphate. None of the hypotheses so far advanced accounts for this difference satisfactorily; the roots of different plants would appear to possess in widely differing degrees, whether by root excretions or otherwise, the power of utilising insoluble phosphates.

[44] *Soil Sci.*, 1926, **21**, 425; **B.**, 763. [45] *Ibid.*, 1923, **16**, 367.

Papers on this subject have also been published by M. Domontovitch,[46] G. Ingham, [47] E. Truninger [48] and E. Ungerer.[49]

Supply of Bases.—In continuation of his investigations into the factors controlling the concentration and composition of the soil solution,[50] J. S. Burd [51] has published a paper dealing with the concentration of cations in the soil solution as determined by biological processes. Using the displacement method of obtaining the soil solution, he has followed the rate at which the concentration of cations is re-established after the original soil solution has been replaced by water. The amount of cations present is determined by the amount of anions formed by oxidative processes. In soils rich in nitrates, the concentration of calcium and other cations is largely determined by the nitrate content, but when this is reduced to a low value by absorption by plants or otherwise, other anions, notably the bicarbonate anion, take the place of the nitrate. Variations in the nitrate content of soils are thus no indication of variations in the content of cations. F. W. Parker and W. W. Pate [52] have studied the relation between the state of saturation of the soil with calcium ions, which is correlated with its hydrogen-ion concentration, and the "availability" of calcium, determined by its ease of replacement by potassium acetate solution. They show that the availability is lowest in soils of high hydrogen-ion concentration and *vice versa*, although they have not investigated the relationship between the availability so determined and the response to liming obtained in vegetation experiments with the same soils.

The injurious action of heavy applications of lime on some soils has been investigated by E. W. Bobko, B. A. Golubev, and A. F. Tulin.[53] This action cannot be ascribed to a development of alkalinity, since both on very light soils and on heavy soils the p_H value was raised to about the same figure, 8, but only on soils of the former type was the harmful effect observed. They ascribe this effect to the development of excessive biological activity with the production of excessive concentrations of calcium, bicarbonate, ammonia, nitrate and sometimes nitrite ions; these products attain a higher concentration in the light soil owing to its lower absorptive

[46] *Contrib. Sci. Inst. Fertilisers, Leningrad Bull.*, 1924, **12**, 141; **A.**, 1926, 762.

[47] *S. Afr. J. Sci.*, 1925, **22**, 122; **B.**, 1926, 840.

[48] *Landw. Jahrb. Schweiz.*, 1925, **39**, 807; **B.**, 1926, 415.

[49] *Z. Pflanz. Düng.*, 1926, *A*, **7**, 352.

[50] *Ann. Report*, 1923, **20**, 208.

[51] *Soil Sci.*, 1925, **20**, 269; **B.**, 1926, 101.

[52] *J. Amer. Soc. Agron.*, 1926, **18**, 470.

[53] *Z. Pflanz. Düng.*, 1925, *A*, **6**, 128; **B.**, 1926, 1024. See also *Ann. Report Appl. Chem.*, 1925, **10**, 447.

capacity. The harm seems to be done mainly by the accumulation of ammonia, since the symptoms disappear as soon as the ammonia is nitrified or washed out.

The relation between the supply of manganese to the plant and lime-induced chlorosis is shown by the results of E. Gilbert, F. T. McLean, and L. J. Harden.[54] These workers found that chlorosis which occurred only on heavily-limed soils was associated with a lower manganese content of the plant and could be cured by the application of manganese either to the soil or sprayed in solution on the plant; the application of iron in various forms had no effect. J. S. McHargue [55] maintains that manganese is particularly concerned in the synthesis of chlorophyll. Clausen [56] records the prevention of "yellowing off" of oats by treatment of the soils with manganese. T. Wallace and C. E. T. Mann,[57] from an analysis of the leaves of chlorotic fruit trees, find a higher percentage of calcium and potassium in these leaves compared with those of healthy trees. These results are contrary to those recorded by other workers on lime-induced chlorosis, but are in agreement with those obtained by H. Colin and A. Grandsire [58] in an investigation of congenital chlorosis or albinism.

Attention is also directed to the investigations of W. Elliott, J. B. Orr, T. B. Wood, A. Crichton, W. Godden, and E. M. Cruikshank [59] on the mineral content of pasture grass and its effect on herbivora. The principal bearings of this work are on the question of animal nutrition, but the results are also of interest with regard to plant nutrition. Samples of herbage from natural pastures of considerable variation in feeding quality do not differ appreciably in their content of energy material, but marked differences in their content of ash constituents are found, these differences being correlated with their feeding quality. The ash content of the herbage rises to a maximum during the summer and then falls. The influence of mineral manures is clearly traceable in the ash content of the herbage.

The Toxic Aluminium Hypothesis of Infertility of Sour Soils.

For some years past, much attention has been devoted to the presence of soluble aluminium compounds in acid soils and the rôle of aluminium in soil infertility and toxicity.[60] F. Hardy [61] has

[54] *Soil Sci.*, 1926, **22**, 437.
[55] *Ind. Eng. Chem.*, 1926, **18**, 172; **A.**, 438.
[56] *Deuts. Landw. Presse*, 1926, **53**, 326.
[57] *J. Pom. Hort. Sci.*, 1926, **5**, 115.
[58] *Compt. rend.*, 1925, **181**, 133. [59] *J. Agric. Sci.*, 1926, **16**, 59.
[60] See *Ann. Reports*, 1922, **19**, 213; 1923, **20**, 218; 1924, **21**, 182; 1925, **22**, 205. [61] *J. Agric. Sci.*, 1926, **16**, 616; **B.**, 1024.

published a critical review of the present position of the subject. The following summary is largely based on that review.

When acid soils are extracted with solutions of neutral salts, as in the estimation of soil acidity by some of the proposed methods, considerable quantities of aluminium as well as iron and manganese are found in the extract. Aluminium in acid soils was regarded as the cause of their infertility, and soil acidity came to be looked upon as a merely secondary consequence of the known susceptibility of aluminium salts to hydrolysis. Subsequent work showed that aluminium could be detected by ionic reactions in soil extracts only when their hydrogen-ion concentration was higher than that corresponding to p_H 4·5 (Rice). It was therefore assumed that in less acid soils and extracts the soluble aluminium occurred as un-ionised hydrated alumina hydrosol. The demonstration of the inability of the aluminium in acid soils and extracts to pass through semipermeable membranes was held to support this view. It was then maintained that, so far from soil acidity being a consequence of the hydrolysis of aluminium salts, the reverse was the case; ionised aluminium was supposed to occur only when the acidity of the soil or extract was sufficient to convert the un-ionised hydroxide into an ionised salt (Denison). The recent work of Magistad has added considerably to our understanding of the position. He studied (*a*) the influence of hydrogen-ion concentration on the solubility of aluminium originally present as sulphate, (*b*) the amount of aluminium in soil solutions displaced from soils of various reactions, and (*c*) the state of occurrence of aluminium in soil solutions. He showed that, between the p_H limits of 4·7 and about 8, only very small amounts of aluminium existed in solution, either in simple aqueous solutions derived from aluminium sulphate or in displaced soil solutions, and that these small amounts existed in colloidal dispersion and not in true molecular or ionic solution. He therefore concluded that aluminium should not exert toxic effects on plants unless the reaction of the medium lay outside the range of p_H 4·7—8·5. This was supported by vegetation experiments in sand at various p_H values in presence and in absence of aluminium. Although certain species of plant showed some sensitiveness to aluminium toxicity, this was never strong at reactions less acid than p_H 5, and most plants showed much more sensitiveness to hydrogen ion than to aluminium.

Hardy goes on to discuss the position in regard to recent work on the physico-chemical properties of hydrated alumina, with special reference to its isoelectric point and the formation of co-ordinated complex anions and organo-compounds. Soluble aluminium in both these forms, as well as in the form of simple ions

or more complex colloidal electrolytes, may possibly penetrate plant root cells and be translocated within the plant, but it appears to exert true toxic effects only when existing as simple ions or the more soluble colloidal electrolytes; absorption of aluminium in other, non-toxic, forms may result in the accumulation of aluminium in certain regions of the plant, with consequent disturbance of metabolic processes and predisposition to certain diseases. The use of dialysis experiments, which has contributed to the above views, is questionable, since dialysis disturbs the equilibrium conditions in hydrated colloidal systems and since dialyser membranes do not simulate plant cell membranes. However, there is considerable evidence derived by other means to support the conclusion that within the reaction range at which toxic aluminium compounds cannot exist in soils—a range which includes that of the reactions of most soils—hydrogen ions may exert a controlling influence on plant growth. It is, however, inadmissible to apply in this connexion a strict reaction range to all soils; moreover, the variations in the sensitiveness of different species of plants must not be disregarded.

The recently published work of J. Line [62] is in full accord with the main conclusions outlined above. He could find only very small amounts of soluble aluminium in acid soils, and could not correlate these amounts with crop yields from these soils. In addition to the direct toxic effect of hydrogen ion above certain concentrations, the precipitation of phosphates, with consequent phosphate starvation of the plant, may be responsible for the harmful effects wrongly attributed to the direct effect of aluminium in solution cultures (compare Gile, Magistad).

The Penetration of Salts into Plants, and their Inorganic Nutritive Requirements.

In addition to the large numbers of papers on the toxic or stimulating action of various inorganic salts on plant growth and on the penetration of various ions into plant-tissues, special mention must be made of the work of D. R. Hoagland and his co-workers and of W. F. Gericke. The former, in collaboration with P. L. Hibbard and A. R. Davis,[63] has continued his investigations on the influence of light, temperature, and other conditions on the ability of the cells of *Nitella* to concentrate halogens in the cell sap. It has been shown that this fresh-water alga can absorb bromine from very dilute solutions containing bromide, without damage to the cells, until the concentration of bromine inside the cell may be

[62] *J. Agric. Sci.*, 1926, **16**, 335; **B.**, 891.
[63] *J. Gen. Physiol.*, 1926, **10**, 121.

nearly sixty times that in the surrounding medium. This absorption does not occur in the dark, light being essential to the process, the temperature coefficient of which is comparable more with that of a chemical reaction than with that of a diffusion process. The process may take a month or more to reach equilibrium. Chlorine may be lost from the cell as a result of the accumulation of bromine, or *vice versa*, but both these elements may accumulate together to concentrations much higher than those in the surrounding liquid.

Osterhout [64] has recently advanced the view, from work on the absorption of carbon dioxide or hydrogen sulphide by *Valonia*, that the penetration of living protoplasm is confined to undissociated molecules, ions being unable to enter. Whilst this view is supported by the work of M. Irwin [65] on the absorption of brilliant-cresyl-blue by *Nitella*, M. M. Brooks [66] could find no evidence for it from her results with *Valonia* and solutions of arsenic or arsenious acids. Hoagland, Hibbard, and Davis prefer to interpret their results as involving the absorption of ions, in view of the very dilute solutions employed and from other considerations. They direct attention to a number of points of dissimilarity between Osterhout's results and their own which throw doubt on the applicability of the former's views to the processes they have studied.

W. F. Gericke,[67] who has already published preliminary accounts of his experiments on the nutrient requirements of wheat at different stages of growth, has now published fuller details. It is known that the greater part of the absorption of inorganic elements by cereals occurs in the earlier part of their growth, the later stages being most marked by elaboration and translocation of organic materials inside the plant. Gericke has attempted to ascertain to what extent the plant could therefore be deprived of certain nutritive elements in the later stages of its growth without detriment. Working with water cultures, he made the rather surprising discovery that when plants were grown for the first few weeks in a complete nutrient solution and then transferred, when they had made only a small fraction of their total growth, to a solution deprived of either potassium, magnesium, sulphur, or phosphorus, they produced markedly more grain and straw than did plants grown to maturity in the complete nutrient solution. When the plants were deprived of phosphorus after 4 weeks, they produced nearly 50% more straw and more than $2\frac{1}{2}$ times as much grain as when they were supplied

[64] W. J. V. Osterhout and M. J. Dorcas, *J. Gen. Physiol.*, 1925—1926, **9**, 255; W. J. V. Osterhout, *ibid.*, 1925—1926, **8**, 131.

[65] *Ibid.*, 1926, **9**, 561; **A.**, 647.

[66] *Amer. J. Physiol.*, 1926, **76**, 116; **A.**, 645.

[67] *Bot. Gaz.*, 1925, **80**, 410.

with this element throughout their growth. Calcium, iron, and nitrogen, however, are needed apparently for most of the period of growth; deprivation of the plants of these elements at any period of the growth up to ten weeks from the commencement caused a diminished yield of grain and straw. No explanation has yet been advanced for these interesting results, which would, however, appear to have important bearings on the relation of soil conditions to crop production.

Synthesis and Metabolism of Carbon Compounds in Plants.

The occurrence of aldehydes in plants and their rôle in metabolic processes are attracting much attention, but interest has shifted from formaldehyde to acetaldehyde. The occurrence of the former as a step in the photosynthetic process now seems to be definitely established. G. Klein and O. Werner [68] have isolated it from various plants by means of "dimedon" (dimethyldihydroresorcinol). It was obtained only from tissue containing chlorophyll, which was exposed to light. Narcosis with phenylurethane or the presence of hydrogen cyanide resulted in its absence. T. Sabalitschka and H. Weidling,[69] in continuation of their work on formaldehyde assimilation by plants, have shown that the aquatic plant *Elodea canadensis* can polymerise formaldehyde to higher carbohydrates irrespective of whether the plant is illuminated or not. The optimum concentration of formaldehyde in the liquid is 0·024%. The same authors [70] have obtained similar results with acetaldehyde, the optimal concentration in this case being 0·032%. G. Klein and K. Pirschle,[71] also using dimedon, have demonstrated the presence of acetaldehyde in actively respiring organs of plants and in roots and leaves. K. Pirschle [72] has found relatively large quantities in germinating seeds rich in fat. He considers that it is probably formed during the utilisation of dextrose from the fat of the seeds, but it may also be an intermediate stage in the conversion of fat into sugar. C. Neuberg and A. Gottschalk,[73] and also J. Bodnár, C. Szepessy, and J. Ferenczy,[74] have found alcohol as well as acetaldehyde in germinating seeds, in relative amounts supporting Neuberg's view that acetaldehyde is an intermediate product in alcoholic fermentation of sugar.

P. Haas and T. G. Hill [75] have continued their study of the water-

[68] *Biochem. Z.*, 1926, **168**, 361; **A.**, 439.
[69] *Ibid.*, 1926, **172**, 45; **A.**, 871.
[70] *Ibid.*, 1926, **176**, 210; **A.**, 1182.
[71] *Ibid.*, 1926, **168**, 340; **A.**, 439.
[72] *Ibid.*, 1926, **169**, 482; **A.**, 547.
[73] *Ibid.*, 1925, **160**, 256; **A.**, 1926, 98.
[74] *Ibid.*, 1925, **165**, 16; **A.**, 1926, 438.
[75] *Ann. Bot.*, 1925, **39**, 861; 1926, **40**, 709; **A.**, 1926, 99, 1066.

soluble chromogen—" hermidin "—isolated from *Mercurialis*. The oxidation of this chromogen to the blue pigment " cyanohermidin," and thence to the yellow " chrysohermidin " is not due to enzyme action. Equal amounts of oxygen are required for the two stages. The process is reversible, the yellow pigment being reduced to the blue and thence to the chromogen by the aluminium–mercury couple, whilst hermidin itself can effect the first stage of the reduction. It is suggested that hermidin plays some part in the oxidation mechanism of the plant. R. K. Cannan [76] has measured the electrode potentials of the system hermidin–cyanohermidin.

Nitrogenous Metabolism and Constituents of Plants.

The relation between calcium supply and protein content of leguminous plants, to which reference has been made in recent Reports, has been further studied by J. M. Ginsburg and J. W. Shive.[77] Working with soy-beans in soil and in water-cultures, they found that variations in the supply of calcium in the form of nitrate or chloride had no significant effect on nitrogen uptake, but the presence of calcium carbonate definitely increased the nitrogen content of the plant. Since, however, this was always to be correlated with lower hydrogen-ion concentration in the medium, it is possible that the latter factor is the determining one and that the effect of calcium carbonate is due to its influence in reducing the hydrogen-ion concentration. Moreover, the view that calcium supply caused increased protein synthesis is not supported by their results, since the increased nitrogen content of plants grown in the presence of calcium carbonate was wholly due to an increase in the non-protein nitrogen.

The complete inadequacy of our knowledge of the composition of the cell sap of plants is the chief hindrance to a better understanding of the processes involved in protein synthesis and nitrogenous metabolism. The work of H. B. Vickery [78] and his associates in Osborne's laboratory at New Haven, to which brief reference was made last year, marks the beginning of an attempt to improve our knowledge in this field. The most widely occurring soluble nitrogen compound in plants appears to be asparagine, which is often regarded as the chief form in which nitrogen compounds are translocated.[79] Vickery's results show that this substance is the most important

[76] *Biochem. J.*, 1926, **20**, 927; **A.**, 1183.

[77] *Soil. Sci.*, 1926, **22**, 175; **B.**, 959.

[78] *J. Biol. Chem.*, 1925, **65**, 657; **A.**, 1926, 99. See also *Ann. Report*, 1925, **22**, 212.

[79] *Ann. Report*, 1924, **21**, 190. See also A. Tokarewa, *Z. physiol. Chem.*, 1926, **158**, 28; **A.**, 1183.

simple constituent among the soluble nitrogen compounds in lucerne. A number of other amino-acids have been isolated from the hydrolysis products of the soluble nitrogen compounds, including serine and alanine, which have not hitherto been recorded as constituents of plant juice. Vickery [80] has also commenced a study of the simpler nitrogenous constituents of yeast; the basic substances not precipitated by Neuberg's reagent consist largely of choline and nicotinic acid. Yeast appears to be incapable of methylating nicotinic acid, and bases of the betaine type, if present, can occur in only very small proportions. R. Fosse [81] claims to have demonstrated the presence of allantoic acid in extracts of *Phaseolus* and suggests that the urea produced on heating extracts of some plants is formed by hydrolysis of allantoic acid. T. Sabalitschka and C. Jungermann [82] have followed the variations in alkaloid content of *Strychnos nux vomica* during germination and early growth. Initially decomposition of the alkaloid appears to occur, but later a resynthesis takes place, the nitrogen being apparently derived from the reserve protein of the seed.

O. Loew claims to show that the protein present in the cells of growing plants exists in a very labile form differing in structure from the stable modification which can be isolated from the plant. A. C. Chibnall and C. E. Grover,[84] in commencing a study of leaf cell cytoplasm, have investigated the soluble proteins which pass readily into solution when the leaves of plants are extracted with water. They resemble glutelins in their properties and their isoelectric point lies between p_H 4·0 and 5·0, in which range their solubility is at a minimum. In all cases, the leaf cell-sap had a p_H higher than the above range, indicating that the protein exists in the cells in the form of anions. Soluble protein could not be obtained from the leaves of plants of which the leaf cell-sap was not alkaline with respect to the isoelectric range. F. A. Csonka, J. C. Murphy, and D. B. Jones [85] have examined a number of vegetable proteins by a modification of Sörensen's method. The more soluble proteins had lower isoelectric points and required more ammonium sulphate for salting-out. The isoelectric points of globulins from different sources were very close together; the same is true of the albumins and prolamins.

[80] *J. Biol. Chem.*, 1926, **68**, 585.

[81] *Compt. rend.*, 1926, **182**, 869; **A.**, 548.

[82] *Biochem. Z.*, 1926, **167**, 479; **A.**, 440.

[83] *Chem.-Ztg.*, 1926, **50**, 429; **A.**, 871; *Ber.*, 1925, **58**, [*B*], 2805; **A.**, 1926, 439.

[84] *Biochem. J.*, 1926, **20**, 108; **A.**, 441. See also A. C. Chibnall, *J. Amer. Chem. Soc.*, 1926, **48**, 728.

[85] *Ibid.*, p. 763.

T. Tadokoro, Y. Nakamura, and S. Watanabe [86] have made a comparison of the properties of oryzanin preparations from common rice and from glutinous rice. The protein from common rice appears to be more complex than the other, as shown by hydrolysis and also by its greater resistance to decomposition by pancreatin. W. F. Hoffman [87] has isolated from rice a protein, soluble in 70% alcohol, which approximates in composition to the alcohol-soluble proteins of maize. B. Takahashi and T. Itagaki [88] have isolated two globulins from the adzuki bean (*Adzukia subtrilobata*). M. C. McKee and A. H. Smith [89] have isolated two proteins from the edible portion of the cauliflower.

Carbohydrate and Structural Constituents of Plant Tissues.

From *X*-ray analysis of plant fibres, O. L. Sponsler [90] concludes that the wall of the fibre has a lattice structure in which the unit cell has the dimensions 6·10 × 5·40 × 10·30 Å., and contains two $C_6H_{10}O_5$ groups. These cells are supposed to be arranged in units of four in the crystallographic unit. The $C_6H_{10}O_5$ groups appear to be of two types which are arranged alternately in chains. The structure of the fibre as a whole is thought to be that of a series of concentric layers of unit cells.

H. Colin and A. de Cugnac [91] describe the isolation of graminin and tricitin, lævulosans from *Arrhenatherum bulbosum* and *Triticum repens*, respectively. They have no reducing action and on hydrolysis yield only lævulose. Enzymes capable of hydrolysing them are found in the plants from which they were prepared.

W. H. Dore [92] has published a useful review of the present state of pectin chemistry, whilst a monograph on the same subject has been published by R. Sucharipa.[93]

Pectic substances can be divided into three groups, protopectin, pectin, and pectic acid. Protopectin, formerly called pectose, occurs in unripe fruits and other parts of plants and is insoluble. The other forms of pectin are derived from it. Pectin itself, which occurs naturally in the juice of ripe fruits or may be obtained from

[86] *J. Coll. Agric. Hokkaido Imp. Univ.*, 1925, **14**, 129; **A.**, 1926, 1066.
[87] *J. Biol. Chem.*, 1925, **66**, 501; **A.**, 1926, 441.
[88] *J. Biochem.* (*Japan*), 1925, **5**, 311; **A.**, 1926, 1066.
[89] *J. Biol. Chem.*, 1926, **70**, 273; **A.**, 1183.
[90] *J. Gen. Physiol.*, 1926, **9**, 677; **A.**, 760.
[91] *Bull. Soc. Chim. biol.*, 1926, **8**, 621; **A.**, 1066.
[92] *J. Chem. Education*, 1926, **3**, 505.
[93] "Die Pektinstoffe" (Braunschweig), Serger and Hempel, 1925. 188 pp. See also *Ann. Report*, 1925, **22**, 213; F. W. Norris, *Biochem. J.*, 1926, **20**, 993; **A.**, 1183; W. H. Dore, *J. Amer. Chem. Soc.*, 1926, **48**, 232; **B.**, 171; M. A. Griggs and R. Johnstin, *Ind. Eng. Chem.*, 1926, **18**, 623; **B.**, 643; W. Honneyman, *J. Text. Inst.*, 1925, **16**, T., 370; **B.**, 1926, 187.

protopectin by mild hydrolysis, is soluble. Pectic acid is a product of further hydrolysis of pectin; it occurs in over-ripe fruits.

Von Fellenberg showed in 1917 that pectin is the methyl ester of pectic acid and in the same year Ehrlich stated that the carboxyl groups of pectic acid were present in galacturonic acid units. Ehrlich also isolated, by hydrolysis of pectin, a tetragalacturonic acid in which four galacturonic acid groups are condensed with the elimination of three molecules of water. In the production of this substance from pectin, galactose as well as methyl alcohol is split off. Tutin's view that pectin is the dimethyl *iso*propenyl ester of pectic acid, based upon his identification of acetone among the products of saponification of pectin has not been accepted by later workers. Schryver and Haines, from the concordant analyses of pectic acids prepared from four different sources, derived the formula $C_{17}H_{24}O_{16}$. Subsequently Carré and Haines concluded that pectic acid is dibasic, having found that the product isolated by Schryver and Haines was a calcium salt with the formula $C_{17}H_{22}O_{16}Ca$. Quite recently, Nanji, Paton, and Ling have isolated a substance which they regard as the basic unit of pectin and which in their view contains a hexa-ring in which four contiguous galacturonic acid units are combined with arabinose and galactose. A unit of this constitution has the formula $C_{35}H_{50}O_{33}$; it would appear to be identical with Schryver and Haines's pectic acid, with which it closely agrees in elementary analysis. The known fission products of pectic acid can all be accounted for on this basis. Pectin is the corresponding methyl ester. The partly methoxylated intermediate products described by Fellenberg and Sucharipa can be accounted for by assuming that only part of the carboxyl groups is methylated. Norris and Schryver, who have accepted the above hexa-ring structure, conclude that in the original pectic substance of the plant one carboxyl group is free and the other three groups are methylated. Protopectin may be regarded as the result of the condensation of this fourth carboxyl group with other radicals.

Pectin solutions are probably not true solutions but sols; although possibly in some cases the gelatinous precipitates obtained by the addition of salts may be metallic pectates, this method of coagulation appears to be chiefly due to the normal coagulation of a sol by an electrolyte. The action of a small amount of acid on a solution containing pectin and sucrose gives a stable gel, constituting the material of the well-known fruit jellies. With regard to the rôle of pectic substances in plants, these apparently occur mainly as incrustive substances. The middle lamella which cements together adjoining cell-walls consists largely of protopectin. The earlier view that protopectin is a calcium salt of pectin has been questioned

by von Fellenberg and recently Sucharipa has put forward evidence to show that it is a combination between pectin and cellulose, these two substances being liberated in uniform proportions upon hydrolysis of protopectin.

The marked changes in texture which accompany the ripening and over-ripening of fruit may be regarded as due to (*a*) the disruption of the union between cellulose and pectin, to which the firmness of unripe fruit is due, (*b*) the saponification of pectin with resultant complete disintegration of the tissue structure in the over-ripe or rotten fruit.

From the work of Nanji, Paton, and Ling, the synthesis of pectin in the plant may be supposed to occur by the condensation of galactose to a hexa-galactan, which is then oxidised and methoxylated. Von Fellenberg regards pectin as the precursor of lignin; in growing twigs, increase in lignin is accompanied by decrease in pectin, whilst the presence of methoxyl groups in both substances is in favour of their being related. W. Fuchs [94] also regards lignin as a product derived from pectin by loss of oxygen and water.

M. M. Mehta [95] maintains that lignin can be quantitatively liberated from its union with cellulose in wood by heating with 4% sodium hydroxide solution for 1 hour at 10 atmospheres. It can be isolated and estimated by precipitation of the resulting liquid with acid and extraction of the product with alcohol. The substance so obtained is brown and acidic and melts at 170°; it is soluble in dilute alkalis and in dilute alcohol. Earlier preparations (*e.g.*, by Willstätter's method) are regarded as impure. The lignin is thought to be combined as a glucoside in lignocellulose. C. Dorée and E. C. Barton-Wright [96] find that the lignocellulose present in the stone cells of the pear resembles that present in forest woods rather than annual lignocellulose such as that of jute. The stone-cell material contains 80% of lignocellulose, of which three-quarters are cellulose and one-quarter is lignin. About three-quarters of this cellulose appears to be true α-cellulose, the remainder consisting of β-cellulose, which yields 74% of its weight of furfural. The remaining 20% of the stone-cell material consists largely of an alkali-soluble furfuroid which yields, besides furfural, acids of the galacturonic type. This result is of interest in relation to the above-mentioned suggestion of von Fellenberg and of Fuchs regarding the origin of lignin from pectin.[97]

[94] *Brennstoff-Chem.*, 1926, **7**, 302. [95] *Biochem. J.*, 1925, **19**, 958.
[96] *Ibid.*, 1926, **20**, 502; **A.**, 872.
[97] For other papers on lignin, see A. Friedrich and J. Diwald, *Monatsh.*, 1925, **46**, 31; **B.**, 1926, 151; H. Urban, *Cellulosechem.*, 1926, **7**, 73; **B.**, 531; K. Freudenberg and H. Hess, *Brennstoff-Chem.*, 1926, **7**, 351; A. R. Bowen and A. W. Nash, *Fuel*, 1926, **5**, 138; **B.**, 474.

The hemicelluloses of beechwood have been isolated by M. H. O'Dwyer.[98] One of them yields xylose and glycuronic acid on hydrolysis, whilst the other resembles pectin in giving arabinose, galactose and galacturonic acid.

Plant Phosphatides.

P. A. Levene and I. P. Rolf, in continuation of their work on this subject,[99] have further examined the lecithin previously isolated from the soy-bean.[1] They have also isolated a fraction insoluble in glacial acetic acid, resembling the cuorin described by Erlandsen in 1907, yielding on hydrolysis palmitic, stearic, linoleic and linolenic acids, aminoethanol, and barium glycerophosphate. V. Grafe and H. Magistris [2] have further studied the water-soluble phosphatides of plants. These appear to occur in the dialysate from Norwegian peas in combination with pigment and carbohydrate groups. By extraction of the peas with warm alcohol, the phosphatide could be obtained free from these substances. The phosphatide complex present in water dialysates of plant foodstuffs is thought by these authors to possess vitamin activity.

Frost Resistance of Plants.

Earlier work carried out by R. Newton has shown that on the approach of winter there is an accumulation of hydrophilic colloids and of sugars in wheat plants. The hydrophilic colloids increase the water-retaining powers of the tissues and the sugars tend to stabilise the proteins against frost denaturation. Newton has now published, in conjunction with W. R. Brown,[3] the results of a more comprehensive study of this subject, in which the changes occurring in winter wheat plants, of varying degrees of hardiness, have been followed during the autumn and winter months. By analysing the press juice as well as the entire tissues, at intervals throughout the investigation, it was possible to study the distribution of the constituents between the cell contents and the supporting framework. The most important adaptation to the onset of wintry conditions is the reduction of moisture content, which takes place to the greatest extent with the hardiest varieties, the resulting concentration increasing the resistance to freezing. The bulk of the colloids in the cell contents consisted of proteins; 90% of the whole protein of the plant was contained in the fluids. Pentosans were found to be restricted almost wholly to the structural parts of the plant.

[98] *Biochem. J.*, 1926, **20**, 656; **A.**, 983. [99] *Ann. Report*, 1925, **22**, 213.
[1] *J. Biol. Chem.*, 1926, **68**, 285; **A.**, 982.
[2] *Biochem. Z.*, 1926, **176**, 266; **177**, 16; **A.**, 1279, 1280.
[3] *J. Agric. Sci.*, 1926, **16**, 522; **B.**, 991.

Concentration of sugar increased most in the hardiest varieties, thus giving them the greatest resistance to frost denaturation of proteins. There was no evidence that lipoids play any important part in the physiology of frost resistance of wheat. The commonly held view, first advanced by MacDougal,[4] that pentosans were of the greatest importance in frost resistance would not appear to be tenable in the case of wheat. Moreover, the work of J. Doyle and Miss P. Clinch [5] indicates that for conifers also there is no apparent connexion between cold resistance and pentosan content of the leaves.

Enzymes.

Space does not permit of a general review of the very large amount of work that is being published on this subject. However, the publication by R. Willstätter of two summaries [6] of the results obtained by him and his collaborators provides a convenient opportunity to take stock of the position in that section of the subject that he has studied during recent years: the methods of isolation and characterisation of enzymes. So many lengthy papers have issued from the Munich laboratory that the task of mastering their contents is formidable, and the opportunity of learning Willstätter's own opinion regarding the most important advances in the subject is a welcome one.

Touching the specificity of enzymes, it is pointed out that, although different proteoclastic enzymes may attack the same substrate, they do so at different atomic groupings. An interesting further development of this is the result recently obtained by R. Kuhn, according to which there are two invertases, which hydrolyse sucrose by attaching themselves to the glucose and lævulose radicals respectively.

Willstätter's method for the isolation of yeast invertase consists in the rapid killing of fresh yeast with ethyl acetate and removal of the cell sap poor in enzyme which separates during the first hour. By autolysis of the residue at neutral reaction is obtained an invertase solution contaminated with only one-tenth or one-twentieth of the yeast material. If the yeast is first allowed to ferment a very weak solution of sucrose, maltose, or glucose, its invertase content can be increased 15—20 times (but not its content of other enzymes). The invertase solution obtained as above from such an invertase-enriched yeast is eight times purer than the best invertin preparations.

The fermentation of a biose by yeast does not follow the course

[4] *Carnegie Inst. Wash.*, Publn. No. 297, 1920.
[5] *Sci. Proc. Roy. Dublin Soc.*, 1926, **18**, 219, 265; **A.**, 1280.
[6] *Ber.*, 1926, **59**, [*B*], 1; **A.**, 321; *Naturwiss.*, 1926, **14**, 937.

supposed by Fischer and Lindner, involving the preliminary hydrolysis to monoses before alcoholic fermentation occurs. Maltose can be fermented by maltase-free yeasts, and yeasts rich in maltase can ferment maltose under such conditions (p_H 4·5) that maltose fission by maltase is impossible.

The quantitative estimation of enzymes is possible if the influence of time, temperature, concentration of substrate, acidity, etc., is studied and these conditions are accurately defined. Special account must be taken of variations in specificity. Thus pancreatic lipase is a powerful fat-hydrolysing agent, but without much action on other esters; for liver lipase the converse is true. One mg. of dried pancreas will hydrolyse as much methyl butyrate as 0·4 mg. of liver, but in saponifying olive oil it is as active as 10 g. of liver. It has not yet been possible to standardise conditions sufficiently in the case of peroxydase to obtain constant results.

In the purification of enzymes great difficulties are met with in the removal of contaminating substances. Chemical methods cannot be used, since the enzyme may be altered. Willstätter has utilised with great success the method of absorption on dry kaolin and other substances. Each step of the process is quantitatively followed. The amount of enzyme absorbed by 1 g. of the absorbent is called the absorption value (*A.W.*). By suitably altering the conditions it was possible to increase the *A.W.* of alumina for invertase from 0·15 to more than 200, at which value 1 g. of alumina held the invertase from 12—14 kg. of fresh yeast, and the weight of the "absorbate" was $2\frac{1}{2}$ g. The absorbed material was not a homogeneous substance, but an enzyme-containing complex. Gels of aluminium hydroxide exist in three forms, α, β, and γ. The γ-form is the most stable, and the strongest absorbent of saccharase. When several enzymes occur together (*e.g.*, pancreas), they can often be separated through selective absorption on different absorbents.

The freeing of an enzyme from its associated impurities has often a marked effect on its specificity. Thus purified trypsin acts only on peptone, histone, and certain prolamines; trypsin and enterokinase act on fibrin, casein, and gelatin, whilst erepsin can act on none of these, but only on simple peptides unattackable by activated trypsin.

Almost all the properties usually ascribed to enzymes belong actually to the accompanying impurities; even the optimum p_H is not a function of the enzyme itself, but depends also on the substrate. Thus carica and pineapple protease hydrolyses fibrin best at p_H 7·2, but gelatin and peptone at p_H 5·0. In these cases, the optimum falls within the isoelectric ranges of the substrates, but in other cases, as in that of human and canine gastric lipase,

the optimum p_H rises with the purity of the enzyme. Unpurified preparations of gastric lipase act best at p_H 5—6, but after absorption on kaolin or alumina the best action is at p_H 8, which is the value for pancreatic lipase. This phenomenon is explained on the assumption that in the purification there is removed a substance that hinders action in alkaline media, and also another that favours action in acid media.

The use of homogeneous enzyme preparations may prove of great value in the study of the constitution of the proteins, as it allows of partial and specific decompositions whereby definite groupings can be identified.

The " molecule " of an enzyme appears to consist of a colloidal carrier and a purely chemically active group. The specificity of the enzyme is vested wholly in this active group, which can apparently be transferred from one colloidal carrier to another. It has not yet been possible to separate the enzyme molecule proper from the colloidal carrier without loss of activity.

Biochemistry of Animals.

Internal Secretions.

Thyroxine.—When last year the Reporter gave an account of Harington's opening researches on the nature of the active principle of the thyroid gland, he had little idea that within twelve months the constitution of that compound would have been revealed and its synthesis effected by one of the most perfectly planned and brilliantly executed investigations that have ever reflected credit on the British School of Biochemistry.

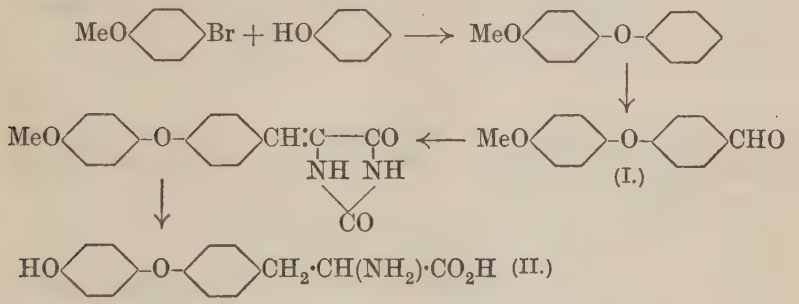
It will be recalled [1] that Harington's synthesis of 3′ : 4′ : 5′-triiodophenylpyrrolidonecarboxylic acid was carried out because the empirical formula is practically the same as that proposed for thyroxine by its discoverer Kendall, and because the properties of the active substance might be more satisfactorily accounted for by the structure of a phenylglutamic acid than by the indole structure put forward by Kendall. The absence of any physiological activity in the product of Harington's synthesis led him to direct a main attack on thyroxine itself.

In the first place, he succeeded in so modifying Kendall's method of isolating thyroxine from the thyroid gland that he obtained yields as high as 0·027%; that is, approximately twenty-five times as large as the yields obtained by the American investigator.[2] Next he established the empirical formula of the purified substance as

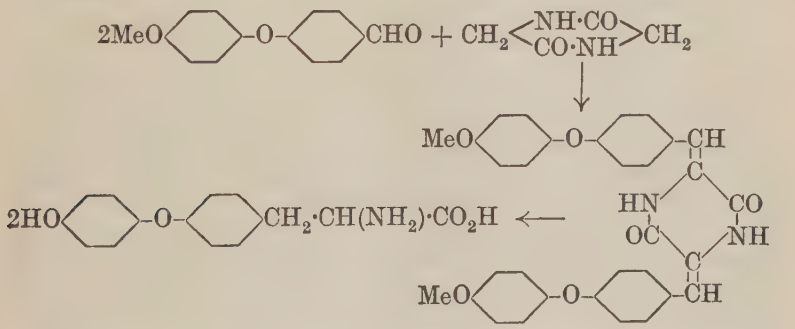
[1] *Ann. Report*, 1925, **22**, 222. [2] *Biochem. J.*, 1926, **20**, 293.

being $C_{15}H_{11}O_4NI_4$, instead of $C_{11}H_{10}O_3NI_3$ derived from Kendall's analyses. The third step [3] was to determine the structure of the molecule, and the evidence accumulating during this part of the study led Harington to believe that the iodine-free substance, deiodothyroxin, was the *p*-hydroxyphenyl ether of tyrosine (II).

Proof of the correctness of this belief was soon provided by the synthesis of this compound and the demonstration of its identity with the product formed by removing the iodine from natural thyroxine. The synthesis was effected as follows:



Alternatively the aldehyde (I) could be condensed with diketopiperazine:



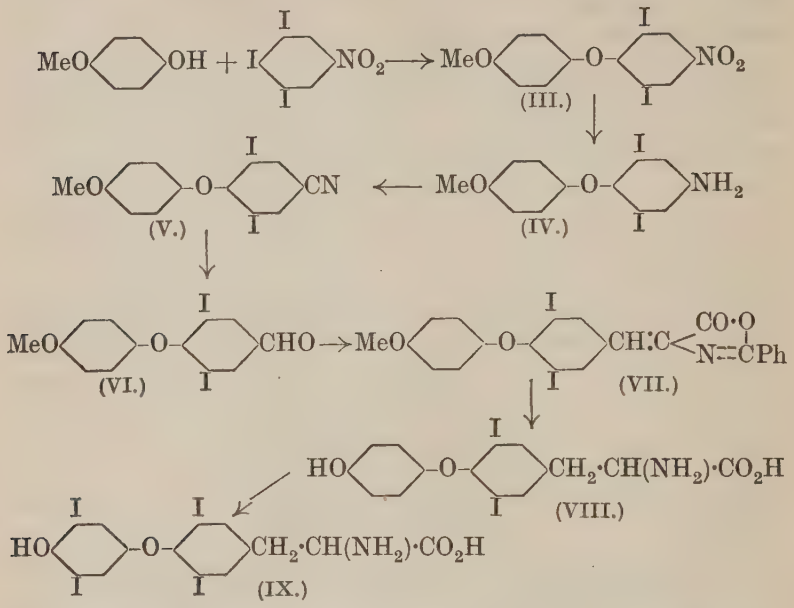
The final stage of this brilliant achievement has just been reported, namely, the insertion of the four iodine atoms and the synthesis of thyroxine itself.[4]

As Harington pointed out in his earlier paper, it seemed probable that the iodine atoms would occupy the 3 : 5 : 3′ : 5′-positions, if for no other reason than the known existence of 3 : 5-di-iodotyrosine in natural products. This surmise has proved to be correct. Quinol monomethyl ether was condensed with 3 : 4 : 5-tri-iodo-

[3] *Biochem. J.*, 1926, **20**, 300.

[4] Report of the meeting of the Biochemical Society (Dec. 5th), *J. Soc. Chem. Ind.*, 1926, **45**, 931.

nitrobenzene to give 2 : 6-di-iodo-4-nitro-4′-methoxydiphenyl ether (III). This was converted through the amine (IV) and the nitrile (V) into the aldehyde (VI), which condensed with hippuric



acid to give the corresponding azlactone (VII). The benzamidocinnamic ester obtained from this, on treatment with hydriodic acid and red phosphorus, gave β-[3 : 5-di-iodo-4-(4′-hydroxyphenoxy)phenyl]-α-aminopropionic acid (VIII). Finally, on treatment with iodine in ammoniacal solution, (VIII) was converted into the tetra-iodo-compound (IX), β-[3 : 5-di-iodo-4-(3′ : 5′-di-iodo-4′-hydroxyphenoxy)phenyl]-α-aminopropionic acid, a substance indistinguishable chemically and physiologically from natural thyroxine.

The intravenous administration of 14 mg. of the synthetic product to two myxœdematous patients in three doses over a period of 6 days caused a rise in the basal metabolic rate from — 45% to + 3% in one case, and from — 32% to — 6% in the other; in both cases, the expected increases in pulse rate and loss of weight were also observed.

West [5] has reported that the related compounds 3 : 5-di-iodotyrosyl-3′ : 5′-di-iodotyrosine and the diketopiperazine corresponding to 3 : 5-di-iodotyrosine are without effect on the basal metabolism.

[5] *Proc. Soc. Exp. Biol. Med.*, 1926, **23**, 629.

Œstrin.—Steady advances are reported in the study of ovarian secretion. Parkes [6] has pointed out that the ordinary cyclic occurrence of œstrus in the adult female mouse is maintained in the absence of follicles and *corpora lutea*, and that there is clear evidence against the view that the responsible hormone, termed by him œstrin, is elaborated by the follicle.

It is also apparent from his researches that œstrin is being constantly produced by the ovary, so that it is necessary to suppose that during pregnancy and lactation, when œstrus does not normally occur, there is an inhibitory action, believed to be exerted through the persistent *corpus luteum*, which prevents the attainment of the threshold concentration of œstrin necessary for the production of œstrus.

Definite evidence of this balanced hormone action is provided by later work [7] in which it is shown that the injection of œstrin during the early stages of pregnancy invariably causes the rapid reappearance of œstrus and the termination of pregnancy; the same effects are produced in the later stages if a larger dose is administered.

The chemical nature of œstrin has been further examined by Ralls, Jordan, and Doisy,[8] who obtained from *liquor folliculi* a fatty material free from cholesterol, of which 0·03—0·04 mg. is 1 rat unit. By fractionation with light petroleum, the unit may be reduced to 0·015 mg. The active principle can be distilled in a high vacuum, but always suffers considerable loss in potency without any gain in purity.

The activity does not withstand acylation or bromination but is unaffected by hydrogenation or hydrolysis. Tentatively, it is suggested that the hormone molecule contains a hydroxyl group and a double bond. Hartmann and Isler [9] confirm the observation that œstrin may be distilled in a high vacuum and state that the active fraction consists of esters of higher unsaturated acids. On saponification, the activity is transferred to a material which distils at 145°/0·02 mm. The preparation of a physiologically active, water-soluble substance of somewhat different properties is described by Laqueur, Hart, de Jongh, and Wijsenbeek.[10] Its relation to the product known as œstrin is not clear, but these authorities regard their preparation, which they term menformon, as a purer form of the active principle.

Secretin.—In a preliminary communication J. Mellanby [11] claims

[6] *Proc. Roy. Soc.*, 1926, [*B*], **100**, 151.
[7] Parkes and Bellerby, *J. Physiol.*, 1926, **62**, 145.
[8] *J. Biol. Chem.*, 1926, **69**, 357; **A.**, 1064.
[9] *Biochem. Z.*, 1926, **175**, 46; **A.**, 1064.
[10] *Proc. R. Akad. Wetensch. Amsterdam*, 1925, **28**, 890; **A.**, 1926, 546.
[11] *J. Physiol.*, 1926, **61**, XXXVII; **A.**, 1064.

to have isolated secretin. His method for its preparation inspires little confidence that anything approaching a pure compound has been obtained, but his products appear to be highly active. On slender evidence, it is suggested that secretin is a polypeptide.

Insulin.—No appreciable abatement of the flood of papers dealing with insulin from one aspect or another is yet apparent, and the task of selecting those most suitable for review is still a formidable one.

With regard to the chemical nature of the active principle of the internal secretion of the pancreas, Funk [12] claims to have isolated insulin by way of its compound with flavianic acid and suggests alternative formulæ $C_{69}H_{102}O_{22}N_{18}S$ and $C_{74}H_{114}O_{24}N_{20}S$, either of which might represent a polypeptide with about 15 constituent amino-acids. Abel [13] has prepared a crystalline compound, of definite melting point (233°), having powerful insulin actions and giving several colour reactions characteristic of protein derivatives. On the other hand, Allen and Murlin [14] claim to have prepared a highly active product which gives none of these colour reactions and therefore could not be of the nature of a peptide. As yet, the evidence in support of these various claims seems confusing.

Passing reference must be made to the rather startling experimental results recorded by Bertrand and Mâchebœuf,[15] although their significance is far from clear. Starting from the discovery that the pancreas of all the species investigated contained, in comparison with other organs, relatively large quantities of nickel and cobalt, and that preparations of insulin itself contain these elements, an investigation was made into the relation between the physiological activity of the pancreas and the presence of the metals. Injection of small doses of nickel or cobalt salts intensified the insulin effect in rabbits and dogs, and it is now claimed that injection or oral administration in human cases of diabetes has sometimes been followed by an alleviation of symptoms.

The much discussed question of the fate of the sugar which disappears from the blood under the action of insulin seems at last to have been answered in a satisfactory manner. The theory [16] that insulin promotes the esterification of blood-sugar with phosphoric acid is not supported by an extension of the work of Burn and Dale carried out by Best, Hoet, and Marks.[17] From this investigation, carefully controlled at all points, it seems clear that the immediate

[12] *Science*, 1926, **63**, 401; **A.**, 1063.
[13] *Proc. Nat. Acad. Sci.*, 1926, **12**, 132; **A.**, 1063.
[14] *Amer. J. Physiol.*, 1925, **75**, 131; **A.**, 1926, 1063.
[15] *Compt. rend.*, 1926, **182**, 1305, 1506; **183**, 5, 257, 326; **A.**, 869, 971.
[16] *Ann. Report*, 1925, **22**, 223.
[17] *Proc. Roy. Soc.*, 1926, [*B*], **100**, 52; **A.**, 870.

effects of insulin in the diabetic are an accelerated combustion of sugar and the synthesis of a further quantity of glycogen. These workers proved conclusively that no significant portion of the sugar which leaves the blood is stored in the muscles as a phosphoric ester and that where excess of sugar is available a large proportion is deposited as glycogen in the skeletal muscles. Insulin hypoglycæmia lasting 1—3 hours does not appreciably reduce the glycogen reserves of the resting skeletal muscles of the preparation of spinal cat, the disappearance of glycogen from the muscles of normal rabbits under the effect of large doses of insulin being chiefly due to the convulsions.

In an attempt to make a balance sheet of the glycogen–sugar system in the insulin-treated animal, Best, Dale, Hoet, and Marks[18] were able to show that the reducing sugar which disappears from an eviscerated spinal preparation under the action of the hormone is equal to the sum of the glycogen deposited in the muscles and the dextrose equivalent of the oxygen absorbed. This balance is preserved whether the blood-sugar is maintained at a high level by the infusion of dextrose or allowed to fall to a low level by restricting the supply. Similar conclusions have been reached by Bessinger and Lesser.[18a]

Much discussion still centres round the question whether insulin "activates" the dextrose molecule by assisting to convert it into a more readily oxidisable form. The original theory of Winter and Smith,[19] after being somewhat generally rejected, was revived a year or more ago in a modified form by Lundsgaard and Holbøll.[20] The latter investigators have during the year under review published several more papers in support of their theory that "new glucose" is formed from α–β-dextrose under the influence of insulin and an essential factor derived from muscle-tissue.[21] Both their methods and the interpretation of their results have been rather severely criticised, for example, by Paul [22] and by Anderson and Carruthers,[23] so the whole question must still be regarded as an open one, particularly in view of the experiments of Visscher.[24]

In connexion with the studies on the nature of the substances that will relieve the symptoms of insulin hypoglycæmia in animals, it is interesting to note that glyceraldehyde is ineffective.[25] In view of

[18] *Proc. Roy. Soc.*, 1926, [*B*], **100**, 55; **A.**, 870.
[18a] *Biochem. Z.*, 1926, **168**, 398. [19] *Ann. Report*, 1922, **19**, 195.
[20] *Ibid.*, 1925, **22**, 224.
[21] *J. Biol. Chem.*, 1926, **68**, 457, 475, 485; **70**, 71, 79, 83, 89; **A.**, 861, 1171. [22] *Ibid.*, 1926, **68**, 425; **A.**, 869.
[23] *Biochem. J.*, 1926, **20**, 556; **A.**, 861.
[24] *Amer. J. Physiol.*, 1926, **76**, 59; **A.**, 536.
[25] Reeves and Hewitt, *J. Physiol.*, 1926, **61**, *Proc.* XXXV; **A.**, 1063.

the disputed position of this substance in the table of normal degradation products of glucose, this evidence is of considerable value, particularly as dihydroxyacetone, on the other hand, serves to restore the blood-sugar level.[26]

The conversion of dihydroxyacetone is, however, according to Mason [27] and also Kermack, Lambie, and Slater,[28] neither rapid nor quantitative. Glucosan and its polymeride, tetraglucosan, are alleged to be of value in the diabetic organism and they have been used to some extent in Germany for treatment. Deuel, Mandel, and Waddell [29] and Winter [30] could find no justification for this practice.

Glucosamine [31] and glutose [32] are of no value in counteracting insulin symptoms, but glucal,[33] possibly because of its ready conversion into mannose, is of service.

Glycolysis.

Much attention has been paid to the phenomenon of glycolysis during the past year and several important papers have appeared. Considerable interest attaches to the experiments of Irving,[34] from which it is deduced that the rate of disappearance of dextrose from an isotonic saline solution in which *erythrocytes* are suspended is independent of the initial concentration, being linear over a wide range of values. The temperature coefficient between 27° and 37° is 2·1. On what appear to be adequate grounds, the conclusion is reached that the degradation of glucose, if not its oxidation, is a surface reaction as far as the corpuscle is concerned and that it does not appear to involve the intervention of an organic phosphorus compound.[34a] Confirmation of the rate of glycolysis being independent of the initial concentration of sugar is provided by Holbøll's experiments on both normal and diabetic bloods.[35] Other studies of the conditions affecting the rate of glycolysis in blood are reported by the last-mentioned investigator [36] and by Brugsch and Horsters.[37]

The fundamentally important nature of the conversion of sugar

[26] Campbell and Hepburn, *J. Biol. Chem.*, 1926, **68**, 575; **A.**, 979.
[27] *J. Canad. Med. Assoc.*, 1926, **16**, 367; **A.**, 1054.
[28] *Biochem. J.*, 1926, **20**, 486; **A.**, 861.
[29] *Proc. Soc. Exper. Biol. Med.*, 1926, **23**, 431.
[30] *Biochem. J.*, 1926, **20**, 668.
[31] Moschini, *Arch. ital. Biol.*, 1924, **74**, 117; **A.**, 1926, 1063.
[32] Benedict, Dakin, and West, *J. Biol. Chem.*, 1926, **68**, 1; **A.**, 754.
[33] Winter, *Biochem. J.*, 1926, **20**, 668.
[34] *Biochem. J.*, 1926, **20**, 613; **A.**, 854. [34a] *Ibid.*, p. 1320.
[35] *Compt. rend. Soc. Biol.*, 1925, **93**, 1684; **A.**, 1926, 1051.
[36] *Ibid.*, p. 1681; **A.**, 1926, 1051.
[37] *Biochem. Z.*, 1926, **175**, 90; **A.**, 1055.

into lactic acid is being emphasised more and more every day. Two years ago, the Reporter directed attention to the studies in Warburg's laboratory on the glycolytic powers of the cancer cell.[38] These results, received at the time with some reserve, seem now to have been adequately confirmed.[39] Rat carcinoma tissue converts some 9% of its weight of glucose into lactic acid aërobically per hour, and sarcoma cells are slightly more active, these glycolytic powers being 60—100 times higher than that of blood.[40] Figures of the same order are given by human tumour tissues.[41]

The inability of the tumour cells to oxidise fully the lactic acid formed by glycolysis is well illustrated by the experiments of Warburg, Wind, and Negelein.[41a] Blood loses about 57% of its glucose in passing through the vessels of a tumour, as compared with 18% on passing through the liver. The inefficiency of the oxidising mechanisms for degrading lactic acid in tumour cells is such that 66% of the glucose that disappears in passing through a tumour appears in the venous blood in the form of lactic acid. Mendel and Bauch question whether the lactic acid thus produced would be sufficient, except in the case of very large malignant growths, to raise significantly the concentration of this acid in the blood.[42] Schumacher suggests, however, that determinations of lactic acid in the blood might be of diagnostic value in certain cases.[43]

In support of the work of Warburg and his colleagues, Bierich has found that the lactic acid content of tumour tissues shows a wide variation, the absolute limits lying about 100% higher than those for normal tissues.[44] Little is yet known of the cause of the lowered oxidation in cancerous tissues. Holmes[45] has found that in general they contain abnormally small amounts of reduced glutathione, and may be slow in reducing the dipeptide added in its oxidised form. Rat sarcoma and carcinoma tissue were found, on spectroscopic evidence, to be deficient in the respiratory pigment cytochrome. Less definite findings are recorded by Bierich and Kalle[46] and by Bierich and Rosenbohm,[47] who conclude that the amounts of reduced glutathione and cytochrome in cancerous tissues may show wide variations, whereas Thomson and Voegtlin[47a] found tumours to be richer in glutathione than most normal tissues.

[38] *Ann. Report*, 1924, **21**, 208.
[39] *E.g.*, Rona and Deutsch, *Klin. Woch.*, 1926, **5**, 1216.
[40] Negelein, *Biochem. Z.*, 1925, **158**, 121.
[41] Stahl and Warburg, *Klin. Woch.*, 1926, **5**, 1218.
[41a] *Ibid.*, p. 829. [42] *Ibid.*, p. 1272. [43] *Ibid.*, p. 497.
[44] *Z. physiol. Chem.*, 1926, **155**, 245; **A.**, 860.
[45] *Biochem. J.*, 1926, **20**, 812; **A.**, 971.
[46] *Z. physiol. Chem.*, 1926, **158**, 1; **A.**, 1169.
[47] *Ibid.*, 1926, **155**, 249; **A.**, 860. [47a] *J. Biol. Chem.*, 1926, **70**, 801.

Lactic Acid and Muscle.

The disturbance of accepted ideas caused by Embden's announcement last year [48] that the liberation of energy due to the formation of lactic acid is not limited to the phase of contraction of muscle has now abated in consequence of a careful re-examination of the question by Meyerhof and Lohmann. Contrary to Embden,[49] they find that the formation of lactic acid is coincident with contraction if moderate stimuli be employed.[50] When, however, muscle is tetanised directly, much lactic acid is liberated during recovery.

Meyerhof has isolated from muscle an enzyme preparation that forms lactic acid from starch or glycogen at a rate about two-thirds of that brought about by the muscle-tissue itself.[51] The preparation may be separated by filtration through a Berkefeld "candle" into two constituents, both of which are essential. It forms lactic acid from hexosephosphates, but at a slower rate than from starch or glycogen—a result that casts some doubt on the intermediate formation of phosphoric esters in this reaction.[52]

Some doubt has been expressed by Deuticke [53] as to the accuracy of the popular view that lactic acid is largely responsible for muscular rigor. According to his view the accumulation of acid leads to changes in the physical properties of the muscle colloids, which, up to a certain point, are reversible. Beyond this point, even although rigor is not yet evident, the change, the inception of which is accompanied by acid production, becomes irreversible and even if some of the acid be removed from the muscle, rigor nevertheless sets in. The changes in the properties of the muscle colloids are exemplified by the inability to esterify phosphoric acid, although the power to hydrolyse hexosephosphate is retained. Muscle in this condition cannot hydrolyse glycogen because of the loss of the power to form the hypothetical intermediate hexosephosphate.

Closely related to these results are those recorded by Hoet and Marks,[54] who investigated the rigor that sets in almost immediately after death from overdosage with insulin or prolonged administration of thyroid. Such rigor is not due to accumulation of lactic or other acid, but the determining factors are the absence of glycogen and a decreased amount of lactacidogen in the muscle. It is suggested that for the appearance of rigor there is needed a disappearance from the muscle of hexosephosphate, probably, as Deuticke suggested,

[48] *Ann. Report*, 1925, **22**, 225.

[49] Embden, Hirsch-Kauffmann, Lehnartz, and Deuticke, *Z. physiol. Chem.*, 1926, **151**, 209; **A.**, 427.

[50] *Biochem. Z.*, 1926, **158**, 128; **A.**, 427.

[51] *Pflüger's Arch.*, 1925, **210**, 790.

[52] *Naturwiss.*, 1926, **14**, 196.

[53] *Z. physiol. Chem.*, 1925, **149**, 259.

[54] *Proc. Roy. Soc.*, 1926, [*B*], **100**, 72.

as a consequence of a failure of the synthetic mechanism. This would occur either from exhaustion of the supplies of raw material, glycogen, or from actual damage or death of the synthetic mechanism itself.

The hypothesis advanced by Foster that there may be two distinct paths by which lactic acid can arise from carbohydrate in the tissues seems now superfluous, since Dudley [55] has shown that the failure to detect glyoxalase in an aqueous extract of rabbit's muscle was due to faulty technique.

Considerable importance must be attached to the experimental results of Burn and Marks [56] in view of the light they cast on the sources of sugar in the body. The livers of dogs or cats that have been fed for some time largely on fat yield, on perfusion with blood of the same species, a reducing substance, presumably sugar, at the rate of 2 to 4 mg. per g. of liver per hour. At the same time, there may be an appreciable formation of glycogen. It has been satisfactorily demonstrated that the sugar does not arise from lactic acid, nor can more than a small fraction be accounted for by the metabolism of protein. It was impossible to obtain clear evidence that there was a disappearance of fat proportionate with the sugar formed, because the total amount of fat was so large and the percentage in different lobes so variable. "Nevertheless," as these investigators remark, "we know of no other source from which the sugar could have come." The production of sugar in these experiments was not obviously influenced by insulin, adrenalin, or pituitary extract.

Biological Oxidations.

Once again it is the duty of the Reporter to devote a considerable proportion of his allotted space to this subject, because the year under review has seen the publication of several papers of outstanding interest.

In the first place, there is the important paper by Cannan, Cohen, and Clark,[57] dealing with the reduction potentials of cell suspensions, which, together with the related study of Clark, Cohen, and Gibbs [58] on the use of methylene-blue as an oxidation–reduction indicator, considers the fundamental questions underlying a vast amount of recent work on biological oxidations, too often inadequately considered by some investigators. The electromotive behaviour of cell suspensions in the absence of foreign reversible systems such as the widely employed methylene-blue shows that electrode measurements

[55] *Biochem. J.*, 1926, **20**, 314; **A.**, 640. See *A.*, 1925, i, 1495.
[56] *J. Physiol.*, 1926, **61**, 497; **A.**, 1055.
[57] United States Health Service Pub. 1926, supp. 55; **A.**, 1009.
[58] *Ibid.*, Reprint No. 1017, 1925.

can be substituted for such indicators and that the electrometric method has obvious advantages, not the least of which is the provision of a continuous record of the full course of the reaction.

In the presence of an indicator such as methylene-blue, titration curves are obtained from which it is possible, by utilising the data from experiments on the dye in pure buffer solution, to deduce the velocity of reduction of the dye by the cell suspension with less trouble and with an accuracy far greater than is possible in such a technique as that described originally by Thunberg. The cell suspension under anaërobic conditions gradually develops a more negative potential, traversing the zones of the series of reversible indicators employed in oxidation–reduction studies by Clark. Should one of these dyes be present, the potentials pass smoothly into the equilibrium potentials of the dye system, the dye is progressively reduced, and the potentials then pass smoothly out of that particular zone.

This behaviour could be explained if one made the reasonable assumption that small quantities of active poising material were being slowly liberated from a large reserve. Tentatively it is suggested by the authors that this represents the " intramolecular adjustments of electronic structures into forms to which the electrochemical considerations may be applied "; in other words, one form of what is now somewhat generally termed " activation " of molecules.

Certain of the facts revealed by this study suggest that there exists a correlation between the characteristic potential and the metabolism characteristic of species, but this question touches on the fundamental problem of the relation that the potentials of a cell suspension bear to conditions within the intact cell, on which as yet little trustworthy information has been gained. The authors of this most interesting paper sound many warnings that should be borne in mind by students of these problems. Not the least important of these is the suggestion that the events of aërobiosis and those of anaërobiosis should be sharply differentiated. The wide span covered by the potentials of anaërobic cell suspensions probably represents a condition entirely distinct from that which exists in the aërobic state, in which it is conceivable that a dynamic equilibrium between reductive and oxidative reactions permits a more or less permanent stabilisation of the system.

If so, there may be, as Needham and Needham think,[59] a definite level of potential inside the living cell.

From these considerations it is obvious that in the " methylene-blue technique " of Thunberg and similar methods of studying

[59] *Proc. Roy. Soc.*, 1925, [*B*], **98**, 259.

anaërobic oxidations, only one narrow part of the whole reducing zone of the cell suspension has been selected.

Since the addition of methylene-blue at once poises the potential of the suspension at a position outside the range of aërated preparations, the question arises as to the relation of events occurring in the presence of methylene-blue and those in the true anaërobiosis of the cell.

Cannan, Cohen, and Clark have also paid some attention to the study of the washed-tissue system so extensively employed by Hopkins and by Thunberg. Exhaustive washing yields a preparation that holds the electrode most erratically, the tendency towards negative potential disappearing as the water-soluble components are removed. The addition of any one of Thunberg's "metabolites" (*e.g.*, succinate) at once causes the electrode to register the typical steady trend towards the negative potential, presumably as activation of their molecules occurs. Washed tissues which fail to reduce methylene-blue still actively reduce 2 : 6-dichlorophenolindophenol and do so after boiling or in the presence of molecular oxygen. The reducing substance can be removed by alcohol extraction and may be, in part, the thermostable "hydrogen donators" described by Hopkins and Meyerhof.[60] These electrochemical studies also confirm the observation that cells contain thermostable "hydrogen donators" capable of reducing glutathione, it being noted in passing that the potentials of the methylene-blue system render it particularly suitable for the study of this particular oxidation–reduction system.

No less important is the stimulating paper by Quastel[61] on a theory of the mechanisms of biological oxidations and reductions deduced from a study of the dehydrogenations produced by resting, that is, non-proliferating, bacteria. As this author remarks, "No very obvious chemical connexion appears to exist between those molecules capable of performing the functions of a hydrogen donator in presence of bacteria or muscle-tissue and it seems necessary, in order to comprehend the activity of these molecules, to resort to a hypothesis which claims that for every such molecule there is, related to it, some specific enzyme." Thus *Bacillus coli* was found to activate 56 substances out of 103 that were examined, and the prospect of having to admit the existence of 56 specific "hydrogen transportases" was sufficient to lead Quastel to question whether some more satisfactory explanation could not be found. In the first place, he examined the question of the site of activation. Obviously this change does not occur in the surrounding medium, since this would postulate that the thermolabile catalysts, for some agent of

[60] *Ann. Report*, 1922, **19**, 189. [61] *Biochem. J.*, 1926, **20**, 166; **A.**, 434.

this type is known to play a part, act extracellularly. On reasonable grounds it is shown that the site of reduction of methylene-blue is probably not in the interior of the cell, so that the conclusion is reached that this change occurs at the cell surface.

If activation of the substrate occurs at a cell interface, not necessarily the surface, the molecule would revert to a "normal" condition when it is out of contact with the structure. On these grounds, it would seem reasonable to assume that the important site of activation is where the reduction of the methylene-blue occurs, namely, at the cell surface.

Based on the theories of orientation of Hardy, Langmuir, and Adams, the author has attempted to picture a cell surface over which are scattered many locally intense electric fields, which, together with the electrical condition of the molecule itself, must, as J. J. Thomson has pointed out,[62, 63] induce "activation" by virtue of their distorting influence on bonds between atom and atom. Thus an acid of the type $A{-}CH{=}CH{-}CO_2H$ may be regarded as assuming the activated form $A{-}\overset{\smile}{C}{-}CH_2{-}CO_2H$, if A be a radical having no directive influence on the movement of the proton; the effect of the carboxyl group (17 electrons) being to produce electric fields at the α-carbon atom, and to a far less extent at the β-atom, that will attract positive electricity. Hence on oxidation, that is, addition of negative electricity, the β-carbon atom will be the one affected.

Thus, for example, fumaric and crotonic acids on activation may be regarded as $CO_2H{\cdot}\overset{\smile}{C}{\cdot}CH_2{\cdot}CO_2H$ and $CH_3{\cdot}\overset{\smile}{C}{\cdot}CH_2{\cdot}CO_2H$, respectively. Therefore, fumaric acid will attract hydrogen because of the field acting at the unsaturated carbon, whereas activated crotonic acid, owing to the effect of the methyl radical, should be less readily reduced and more readily oxidised. Experiments show this to be true.

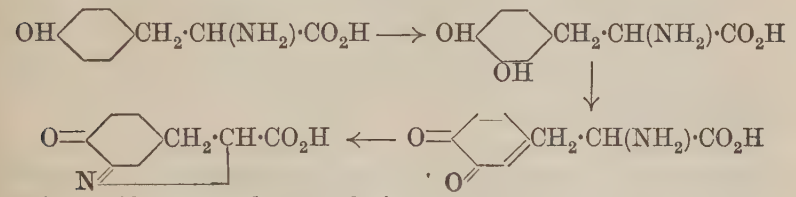
This attempt by Quastel to introduce electrochemical considerations into biochemical oxidation-reductions is noteworthy, and would seem to find experimental justification in the studies of Cannan, Cohen, and Clark already discussed above.

It does not follow that the existence of specific catalysts need be denied. The structure of the cell surface, or, for that matter, of all the cellular surfaces, is an assemblage of inseparable enzymes. It is, however, unnecessary to postulate the existence of a large number of distinct enzyme systems dealing with oxidations and reductions when it is possible to regard specificity of behaviour as belonging to the molecules rather than to the enzymes.

[62] *Nature*, 1923, **112**, 826. [63] *Phil. Mag.*, 1923, **46**, 506; *A.*, 1923, ii, 682.

Bearing on this work and on that of Cannan, Cohen, and Clark, are the observations of Kodama,[64] that hypoxanthine and aldehyde give no reduction potential when activated by xanthine oxydase, but do so in the presence of methylene-blue or oxygen. He states that in the former case the potential is merely that of the dye, whilst in the latter it is that of hydrogen peroxide. The failure to demonstrate the development by activated xanthine at an inert electrode of a reduction potential consistent with its reducing power suggests that we are not yet entitled to generalise from the observations of Cannan, Cohen, and Clark. A better appreciation of conditions governing the behaviour of inert electrodes in such irreversible systems seems to be necessary to further progress in this matter. Xanthine oxidase shows a high degree of specificity towards the hydrogen donator, but, as far as has been ascertained, none towards the acceptor.[65]

Raper [66] has filled in a very important gap in our knowledge of the action of tyrosinase on tyrosine by isolating *l*-3 : 4-dihydroxyphenylalanine in small amounts as a product of the reaction. It is itself rapidly oxidised by tyrosinase to the unstable red pigment previously described,[67] the stages being probably :



(red, unstable compound) ⟶ melanin.

The conversion into melanin is believed to be a simple rearrangement, because this substance contains almost the same percentage of nitrogen as its red precursor.

The isolation of 3 : 4-dihydroxyphenylalanine is an important step, for it not only places on a firm basis the experimental work of Bloch [68] on pigment formation in skin, but overcomes an obstacle which previously made one hesitate to accept the view that tyrosine is the parent substance of adrenaline.

Closely related to these studies are the remarkable results of the investigations of Harrison and Garrett [69] on the induction of melanism in certain moths. Observation of these species, of which

[64] *Biochem. J.*, 1926, **20**, 1095; **A.**, 1175.
[65] *Ibid.*, p. 703; **A.**, 977.
[66] *Ibid.*, p. 735; **A.**, 977.
[67] Compare *Ann. Report*, 1925, **22**, 235.
[68] *Z. physiol. Chem.*, 1916—17, **98**, 226.
[69] *Proc. Roy. Soc.*, 1926, [*B*], **99**, 241.

Silenia bilunaria is typical, proved that the moths in the vicinity of large towns are usually darker in colour than those in the country. The obvious explanation that this was due to natural selection not being found adequate, other causes were sought, with the result that the melanism was traced to a constituent of their food. Larvæ reared on plants exposed to the fumes and smoke of factories developed a large proportion of melanic forms, and the actual exciting factor was shown to be small traces of manganese or lead in the sooty deposit on the leaves.

The melanism could be induced with ease by feeding the larvæ on natural fresh food which had been watered with a very dilute solution of manganese sulphate or lead nitrate.

The amazing feature of the results is, however, that, once induced, the melanism is inherited, usually as a Mendelian recessive. The fact that in one species the acquired character was a dominant leads the authors to reject the hypothesis that the melanism was latent.

The Chemistry of Specific Reactions.

In the *Annual Report* for 1923, the Reporter directed attention to the progress that had then been made in the study of the chemical nature of the specific bacterial substances. Further evidence that the specific substances of certain types of organism are either themselves polysaccharides or are intimately associated with such compounds has accrued.

Heidelberger, Goebel, and Avery,[70] in a series of papers, describe the isolation of substances with specific properties from the *E* strain of Friedländer's bacillus and from *Pneumococcus* type II. In both cases the active substances are nitrogen-free, dextrorotatory polysaccharides, yielding mainly glucose on hydrolysis, and with marked acidic properties. Similar results are described by Laidlaw and Dudley.[70a] Heidelberger and his colleagues state that the specific substance of *Pneumococcus* type III is a lævorotatory, nitrogen-free polysaccharide containing glucose and glycuronic acid, whilst that of type I contains nitrogen, possibly, it is suggested, as a nitrogenous sugar derivative linked to galacturonic acid.

Siebert and Long,[71] in a series of papers on the chemical nature of the active principle of tuberculin, have described the separation of a protein with which the activity is associated. By treating this product by Hopkins's method for isolating crystalline ovalbumin,

[70] *J. Exp. Med.*, 1925, **42**, 701, 709, 727; **A.**, 1926, 545.
[70a] *Brit. J. Exp. Path.*, 1925, **6**, 197.
[71] *Amer. Rev. Tuberculosis*, 1926, **13**, 393; **A.**, 1178.

a crystalline product was obtained which gave typical protein reactions and a marked biological reaction in tuberculous animals.[72]

The complex system known to serologists as complement has been examined with considerable care by Gordon, Whitehead, and Wormall.[73] To the recognised three factors, (1) the globulin component (mid-piece), (2) the albumin component (end-piece), and (3) a heat-stable factor usually associated with the globulin fraction, they have added a fourth factor, also thermostable, which is an essential constituent of the hæmolytic system. This fourth factor is associated with the albumin fraction, is inactivated by ammonia, and is not dialysable. Serum that has been inactivated by ammonia retains its opsonic activity, so that the fourth factor may be regarded as playing no part in opsonic action.

Studies of the diffusible and non-diffusible calcium of serum indicate that the latter fraction is connected with complement activity; some parallel may be traced between the calcium content of various fractions and the power to replace or reactivate the ammonia-treated serum. Attempts to reactivate this material by addition of calcium in various forms were, however, unsuccessful. No alteration in dialysable calcium occurs during the inactivation with ammonia.

Hæmoglobin and Related Pigments.

Advances of the first order of importance have been recorded in this field of research during the past year, and encourage one in the view that we are at last gaining a clear knowledge of the chemical structure of these respiratory pigments as well as of their true biological significance. How far our knowledge of hæmoglobin has been extended during the past few years is clearly revealed in the masterly presentation of the subject made before the Chemical Society early in this year by Professor Barcroft,[74] in whose laboratory a large proportion of the advances have been made.

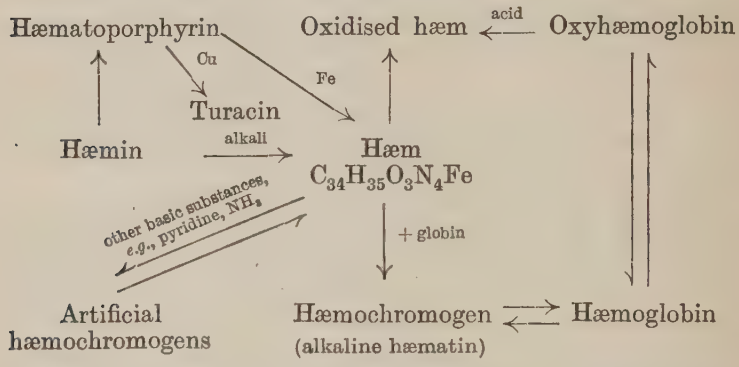
The syntheses of ætioporphyrin and ætiohæmin by Fischer and Klarer from 2 : 3-dimethyl-4-ethylpyrrole is an outstanding event, since they forecast the synthesis of the related dicarboxylic acid hæmatin.[75]

Apart from this narrow gap, the synthesis of hæmoglobin has in one sense been effected, because Hill and Holden have succeeded in combining purified globin with free hæmatin between the p_H limits of 5 and 9 and converting the product into oxyhæmoglobin spectroscopically indistinguishable from the natural substance.[76] The

[72] *Science*, 1926, **63**, 619; **A.**, 1062.
[73] *Biochem. J.*, 1926, **20**, 1028, 1036, 1044; **A.**, 1166.
[74] *J.*, 1926, 1146; **A.**, 750. [75] *Annalen*, 1926, **448**, 178; **A.**, 962.
[76] *J. Physiol.*, 1926, **61**, XXII.

demonstration by Keilin [77] that "acid hæmatin" prepared from oxyhæmoglobin is the same as "oxidised hæm" prepared from hæmin clears up one more point of confusion for which the older nomenclature was to a large extent responsible.

The relation between the blood pigment derivatives may therefore be represented by the following arrangement:



Several points of interest stand out from the recent researches represented by this chart. The combination of the acidic hæm with basic substances of many types to give a variety of hæmochromogens is in itself vastly interesting, but it is indeed remarkable that whereas their formation usually demands a great preponderance of the components, the combination between globin and hæm is almost complete. Moreover, the globin complex is one of the few hæmochromogens that are soluble in high degree, and seems to be unique in its property of passing into hæmoglobin on adjustment of the hydrogen-ion concentration.[78]

The artificial production of metallic compounds of the porphyrins studied in detail by Hill [79] has also revealed many curious points that are of considerable significance from the standpoint of the biological value of hæmoglobin. Many metals—iron, nickel, cobalt, manganese, zinc, copper, silver, potassium, etc.—may be combined with porphyrin to yield compounds which Barcroft would describe as being on the "hæm level." Of these, only three, namely, the complexes with iron, manganese, and cobalt, have the power of being oxidisable and reducible, and only one of these, the iron compound, has a spectrum that suggests hæm rather than hæmochromogen. Furthermore, it is only this one compound that will unite with globin or other basic compounds to yield true hæmo-

[77] *Proc. Roy. Soc.*, 1926, [*B*], **100**, 129; **A.**, 857.
[78] Anson and Mirsky, *J. Physiol.*, 1925, **59**, 50.
[79] *Biochem. J.*, 1925, **19**, 341.

chromogens. This work throws light on the nature of other pigments such as turacin, which is a copper–porphyrin compound incapable of uniting with basic nitrogen compounds and not exhibiting oxidation and reduction reactions.

From a study of the relation between turacin and hæmatin Keilin [80] is inclined to believe that cytochrome may be a modified hæmochromogen compound present in two distinct degrees of dispersion, there being evidence that the α- and β-hæmochromogens described by Anson and Mirsky [81] differ only in their dispersion. Schamm [82] reports a study of cytochrome and the related myohæmatin of MacMunn, in which he confirms Keilin's original observations and traces a relation between the porphyrin of these pigments and α-hæmatoporphyrin.

A very careful and much needed re-examination of the methods employed for measuring the osmotic pressure of hæmoglobin has been made by Adair,[83] who has elaborated a technique that seems above criticism. The osmotic pressure measured on dialysed hæmoglobin by previous investigators ranged from 3·5 to 12 mm.% of protein. Re-determinations by means of the improved method gave values of 3·2 mm. or less, and it has been shown that higher values are obtained only when acid or base remains bound to the protein, or when the experimental conditions are otherwise unsatisfactory.

The smallest possible molecular weight of the pigment being 16,700, Adair's estimate of the value of n as 4 gives an absolute weight of 68,000.

Discussion still centres round the question of the oxygen content of methæmoglobin. Nicloux and Roche [84] maintain that it contains one atom of oxygen less than oxyhæmoglobin and one atom more than hæmoglobin, whereas Conant and Scott,[85] criticising the experimental procedure of Nicloux, assert that methæmoglobin contains only one-fourth as much oxygen as oxyhæmoglobin.

Vitamins.

Vitamin-A.—No progress has been recorded during the past 12 months in the direction of ascertaining the chemical nature of this substance, but Weidemann,[86] during his studies of the substances present in the unsaponifiable fraction of the oil from the livers of

[80] Keilin, *Proc. Roy. Soc.*, 1926, [*B*], **100**, 129; **A.**, 857.
[81] *Ann. Report*, 1925, **22**, 238.
[82] *Z. physiol. Chem.*, 1926, **152**, 55, 147; **A.**, 537.
[83] *Proc. Roy. Soc.*, 1925, [*B*], **98**, 523.
[84] *Bull. Soc. Chim. biol.*, 1926, **8**, 71; **A.**, 750.
[85] *J. Biol. Chem.*, 1926, **69**, 575. [86] *Biochem. J.*, 1926, **20**, 685.

Greenland sharks, *Somniosus microcephalus*, has confirmed the observation of Drummond, Channon, and Coward [87] that neither batyl alcohol nor selachyl alcohol possesses growth-promoting properties.

The colour reactions described by Rosenheim and Drummond,[87] and believed by them to be due to vitamin-*A* and possibly suitable for its quantitative estimation, have been further studied by Carr and Price,[88] whose modifications, employing antimony chloride and an evaluation of the colour by means of the standard glasses of a Lovibond tintometer, are great improvements. Their evidence goes to support the idea that the blue colour is produced from the vitamin.

Fearon [89] has described another colour reaction, given by certain products containing vitamin-*A* on treatment with pyrogallol in the presence of trichloroacetic acid and an oxidising agent. The permanence of the red colour produced seemed at first to indicate that it might be very suitable for purposes of assay, and support for this view was advanced by Willimot and Moore [90] and by von Euler, Myrbäck, and Karlsson.[91]

Further study, however, has revealed that the reaction described by Fearon is not associated with the presence of the vitamin; the chromogenic substance passes, on saponification of an oil in which it is present, into the fatty acid fraction, whereas the vitamin passes into the unsaponifiable residue.[92] The substances responsible for the two colour reactions can thus be separated; moreover, certain substances have been found, *e.g.*, sardine oil, which give a strong Fearon reaction but do not respond to the test with arsenic or antimony chloride. Such products are found to be devoid of growth-promoting activity when tested on animals. The non-specificity of Fearon's test is confirmed by Willimot, Moore, and Wokes.[93]

Vitamin-B.—Ever since the discovery of this dietary factor, or factors, for it is still uncertain whether one or more than one substance is responsible for the physiological action of extracts of yeast, wheat embryo and rice polishings, speculation has been rife regarding its rôle in the animal organism. In one or two directions, there has been a tendency for these speculations to take definite shape, and in none more than in that which views this vitamin as playing an essential part in the oxidative mechanisms of the tissues.

A considerable amount of experimental evidence has been pre-

[87] *Ann. Report*, 1925, **22**, 219. [88] *Biochem. J.*, 1926, **20**, 497; **A.**, 870.
[89] *Ibid.*, 1925, **19**, 888; **A.**, 1926, 207.
[90] *Ibid.*, 1926, **20**, 869; **A.**, 980.
[91] *Z. physiol. Chem.*, 1926, **157**, 263; **A.**, 1181.
[92] *Lancet*, 1926, **11**, 806; **A.**, 481. [93] *Biochem. J.*, 1926, **20**, 1292.

sented in support of this idea, particularly by Abderhalden and by Hess.[94] The latter investigator holds the clear-cut view that the yeast-vitamin is either the mother-substance of the oxidising enzymes or is essential to their formation in the tissues. Abderhalden has not committed himself to so clearly-defined an opinion, but shares with Hess the general view that the oxidative powers of the cell are greatly lowered in the absence of vitamin-*B*.

The main evidence in support of their case is provided by the fact that animals suffering acutely from a deficiency of this vitamin exhibit greatly lowered body-temperature and oxygen uptake. Additional support is derived from experiments which it is claimed demonstrate that isolated tissue and cell suspensions show diminished respiration unless adequate amounts of the vitamin-*B* are added.

The greater part of these studies has been recently submitted to re-examination, with the result that doubt is cast on the accuracy of the conclusions of Hess and Abderhalden.[95] Investigations of the oxygen uptake and oxidising power of suspensions of tissues removed from animals suffering from a deficiency of vitamin-*B* gave results closely agreeing with those obtained with normal preparations.

In studies of the intact animal (rat) confirmation of the fall of body temperature and gaseous metabolism was obtained, but they were observed to occur only shortly before death and to resemble in many ways the similar conditions in the premortal stage of inanition. Comparative examination revealed the fact that starvation plays a very large part in the chain of events that follow a deficiency of vitamin-*B*, because, as Mendel and Cowgill have shown, this dietary principle is related in some essential manner to the complex phenomenon of appetite. In the absence of vitamin-*B* the food consumption falls until the animal is virtually starving, and it remains to be discovered whether there is any other consequence of the deficiency more obscure than this. It must be borne in mind that the greater part of this investigation was carried out on rats, so that the actual relation of the results to the conditions in birds and man known as avian polyneuritis and beri-beri, respectively, is as yet uncertain. In the rats there was no appreciable difference between the nerve lesions noted in vitamin-*B* deficiency and in simple inanition.

Vitamin-D.—In last year's Report an account was given of the interesting and important discovery that highly purified cholesterol, after exposure to ultra-violet radiation, was endowed with anti-rachitic properties similar to those by which the vitamin-*D* has been characterised. Further work reported during the past 12 months

[94] *Z. physiol. Chem.*, 1921, **117**, 284; *A.*, 1922, i, 399.

[95] Drummond and Marrian, *Biochem. J.*, 1926, **20**, 1229.

has maintained the extraordinary interest in this subject. Bills [96] has detected antirachitic powers in the resinous product isolated from cholesterol after boiling with previously ignited fuller's earth in carbon tetrachloride, benzene, or xylene. No active preparations were made when ethyl acetate or various alcohols were used as solvents. In a later paper,[97] he described the isolation of a product, supposed to be $C_{81}H_{138}O_3$, believed by him to be a polymerised cholesterol, which itself possessed no antirachitic properties, but which he considered to be an intermediate product in the formation of the active substance. The evidence he adduces in support of this view is, however, of the slenderest nature.

Rosenheim and Webster,[98] by removing the unchanged cholesterol from the irradiated product by precipitation with digitonin, were able to concentrate the antirachitic activity in the filtrate, their preparation being physiologically protective to rats in doses as small as 0·01 mg. daily. Hess, Weinstock, and Sherman [99] did not at first succeed in effecting this separation, because they irradiated their material in air, whereas Rosenheim and Webster employed an atmosphere of nitrogen; later they were able to confirm the statement that oxidation of the active substance may occur during exposure and result in a reduced yield.[99a]

This fact throws doubt on the correctness of the view of Vollmer and Serebrijski,[1] that the antirachitic activation of cholesterol is essentially a peroxide formation. The uptake of oxygen noted by him and by Hamano [2] seems entirely unrelated to the phenomenon of vitamin formation.

In an attempt to correlate the production of the vitamin with the known structural units of the cholesterol molecule, Rosenheim and Webster [3] have studied a large number of derivatives and related substances—cholesteryl chloride, cholestene, cholestenone, coprosterol, α-amyrol, and the possibly related hydrocarbon squalene (see later) were not rendered antirachitic by ultra-violet light, but active preparations were made from ergosterol and the acetate and palmitate of cholesterol. These facts seem to point to the necessity of the secondary alcohol group and the unsaturated linking being intact before activation can occur. An extension of these studies recently reported has forced the authors to express another

[96] *J. Biol. Chem.*, 1926, **67**, 753; **A.**, 645.
[97] Bills and McDonald, *J. Biol. Chem.*, 1926, **68**, 821; **A.**, 981.
[98] *Biochem. J.*, 1926, **20**, 537; **A.**, 870.
[99] *J. Biol. Chem.*, 1926, **67**, 413; **A.**, 546.
[99a] Hess, Weinstock, and Sherman, *ibid.*, 1926, **70**, 123; **A.**, 1182.
[1] *Biochem. Z.*, 1926, **176**, 84; **A.**, 1181.
[2] *Ibid.*, 1926, **169**, 432; **A.**, 546.
[3] Rosenheim and Webster, *J. Soc. Chem. Ind.*, 1926, **45**, 932.

view, because it was found that a specimen of cholesterol regenerated from the dibromide could not be activated by ultra-violet light. The proffered explanation is that " pure " cholesterol prepared in the usual manner may, even after repeated saponification and recrystallisation, retain traces of an impurity which is the precursor of the vitamin, and for which the name *vitasterol* is proposed. Treatment with bromine irreversibly changes this substance as far as its power to give rise to the vitamin is concerned, so that cholesterol regenerated from the dibromide cannot be activated.

This conclusion confirms that deduced by Heilbron, Kamm, and Morton,[4] from an entirely different line of argument. In repeating the work of Hess and of Schultz and Ziegler [5] on the absorption bands of cholesterol, these investigators observed that the absorption spectrum of " pure " cholesterol was apparently a compound one. By fractional crystallisation of 2 kg. of the raw material they concentrated a least soluble fraction, weighing 5 g., which exhibited three well-defined absorption bands at 293, 280, and 269 $\mu\mu$, whilst the purified cholesterol showed only general absorption in the ultra-violet. These characteristic bands disappeared when this substance was irradiated in alcoholic or ethereal solution, and the suggestion is advanced that such a product is, in view of these properties, more likely to be the precursor of the vitamin than pure cholesterol. In this connexion, it may be recalled that Hess [6] showed some years ago that the curative rays of the spectrum in the direct treatment of rachitic children by light have wave-lengths in the vicinity of 290 $\mu\mu$.

Spermine.

The researches into the constitution of this interesting tissue component reported last year have been continued during the past 12 months. Dudley, Rosenheim, and Starling [7] found that destructive distillation of the hydrochloride yielded pyrrolidine, whilst decamethylspermine sulphide on degradation yielded hexamethylspermine and tetramethyltrimethylenediamine, $NMe_2 \cdot [CH_2]_3 \cdot NMe_2$.

This evidence suggested the presence of the chains N–C–C–C–N and N–C–C–C–C–N in the molecule, which together with the fact that there are two amino- and two imino-groups present suggested two alternative formulæ :

(*a*) $NH_2 \cdot [CH_2]_3 \cdot NH \cdot [CH_2]_4 \cdot NH \cdot [CH_2]_3 \cdot NH_2$ and
(*b*) $NH_2 \cdot [CH_2]_4 \cdot NH \cdot [CH_2]_3 \cdot NH \cdot [CH_2]_3 \cdot NH_2$.

[4] *J. Soc. Chem. Ind.*, 1926, **45**, 932.
[5] *J. Biol. Chem.*, 1926, **69**, 415; **A.**, 1065.
[6] *J. Amer. Med. Assoc.*, 1922, **78**, 1596.
[7] *Biochem. J.*, 1926, **20**, 1082; **A.**, 1128.

The synthesis of the compound (*a*) was accomplished by condensing αδ-diaminobutane (putrescine) with γ-bromo-α-phenoxypropane. Treatment of the resulting αδ-bis[γ′-phenoxypropylamino]butane with hydrobromic acid resulted in replacement of the phenoxy-groups by bromine, and the subsequent action of ammonia gave the required αδ-bis[γ′-aminopropylamino]butane. This compound was found to resemble the natural base in all respects.

Most of the observations reported by Wrede [8] agree with the formula established by Dudley, Rosenheim, and Starling. The same investigators have also examined the constitution of a related base, termed spermidine, which accompanies spermine in extracts of animal tissues.[9] This substance appears to be

$$NH_2\cdot[CH_2]_3\cdot NH\cdot[CH_2]_4\cdot NH_2$$

and its synthesis has been achieved.

J. C. Drummond.
H. J. Page.

[8] *Z. physiol. Chem.*, 1926, **153**, 291; **A.**, 751.

[9] Report of the Meeting of the Biochemical Society, Nov. 8th, 1926; *J. Soc. Chem. Ind.*, 1926, **45**, 839.

CRYSTALLOGRAPHY.

Sections of the subject which have been selected for special treatment in this Report are "The Dynamics of the Crystal Lattice" and "The Intensity of *X*-Ray Reflexion." The former has not been dealt with in the Annual Reports for several years and considerable progress has been made, although our knowledge of the forces between atoms is still so fragmentary. The immense importance to chemistry of a precise examination of the forces in crystals need hardly be emphasised. A discussion of the "Intensity of *X*-Ray Reflexion" has been included in this Report on crystallography, because the successful examination of crystalline structure is dependent on a knowledge of the laws which govern reflexion. Every advance in this knowledge implies a correspondingly greater power of examining the finer details of structure. In order to keep the Report within the allotted length, certain other aspects have been touched on very briefly. The structures of metals and alloys, and the study of imperfectly crystallised bodies have been dealt with recently and do not form the subject of special sections in the present Report.

"Die Verwendung der Röntgenstrahlen in Chemie und Technik,"* by Hermann Mark, will be welcomed by crystallographers. Mark writes with authority, for he has won general recognition as a most distinguished experimentalist amongst those who are investigating crystalline structures in Germany. The book is a valuable addition to the existing literature, because the author's point of view differs from that adopted in other well-known books. Mark devotes much space to the technique of *X*-ray analysis, and to the technical application of the results which can be obtained, the book being designed for the use of those who are engaged in industrial research.

The article on "*X*-Ray Diffraction Data from Crystals and Liquids" in the International Critical Tables, by R. W. G. Wyckoff, contains a valuable summary of experimental observations. It is regrettable that the author has, in these International Tables, replaced the time-honoured Schoenflies notation of space-groups by one which he has devised himself, for although Schoenflies's notation is not ideal and more consistent systems might be found, it has

* "Handbuch der Angewandten Physikalischen Chemie," Bd. XIV, Barth, Leipzig.

the merit of being universally accepted and is familiar to all crystallographers. It would be preferable to examine alternative notations very thoroughly and to obtain a general consent before replacing Schoenflies's historical terminology, as it is of prime importance to avoid the confusion caused by several systems. The structures are so described in the tables that the atomic positions can be found by consulting Wyckoff's book, "The Structure of Crystals," as a key. A striking feature brought out by the tables is the simplicity of the compounds which have as yet been analysed at all completely, and the small number of crystal types which account for the majority of forms. It emphasises the limitations of the new science, which has as yet succeeded in mastering so few of the more complex structures.

An article on the structures of solids and their analysis by *X*-rays by P. P. Ewald * has recently appeared in the "Handbuch der Physik" series. The article describes the standard methods of analysis and summarises the results. It is no easy task to select from the large number of published analyses those which may be relied on with confidence, and to judge to what extent these analyses are definite and where they become speculative. Ewald gives a very good critical review of the subject, illustrating the structures with excellent figures. The introduction to the study of crystal symmetry is well planned to help the student, giving all the necessary ideas while being much less formidable than the treatment by other authors.

Crystalline Symmetry and Etch-Figures.

K. F. Herzfeld and A. Hettich [1] have studied the etch-figures of sylvine, potassium chloride. If their conclusions are substantiated, it will be necessary to revise accepted ideas about the relationship between the symmetry of a crystalline structure and the external symmetry displayed by the crystalline faces, or by etch-figures. Sylvine has been assigned by the mineralogist to a hemihedral (holoaxial) class of the cubic system because the four-sided figures which appear when a cube face of the crystal is etched are often twisted from the symmetrical position, and all in the same direction. Herzfeld and Hettich claim (1) that all potassium chloride crystals of a crop etched by the same solvent show figures twisted in the same sense, whereas one would expect half the crystals to be right-handed and half left-handed; (2) that when precautions are taken against all contamination by impurities, particularly by organic

* "Handbuch der Physik," Band XXIV, pp. 191–369. Springer, Berlin.

[1] *Z. Physik*, 1926, **38**, 1; A., 889. See also A. Hettich, *Z. Krist.*, 1926, **64**, 265.

matter, the etch-figures are always symmetrical. They conclude that *the asymmetry is to be traced to impurity in the etching fluid, not to the crystal structure.* If a trace (0·1 mg.) of optically active amyl alcohol be added to the purified system, the etch-figures are greatly increased in number and again indicate holoaxial symmetry by being twisted. Similarly, if a crystal which only shows symmetrical figures be removed from the solution, touched with the finger, and replaced, unsymmetrical figures appear. The lowering of symmetry is ascribed to small traces of organic matter which has the asymmetry of an optically active substance, and is absorbed on the crystal face. J. J. P. Valeton [2] criticises these conclusions, and denies that two faces of a crystal which belong to the same form can be acted on differently by a foreign body. It appears, however, that Herzfeld and Hettich are justified in drawing their conclusion that this difference is possible. Two faces of a crystal derived from each other by a symmetry operation of the first sort, such as rotation about an axis, must be identical in all respects, but two faces related by an operation of the second sort (reflexion) present surfaces which are the mirror images of each other as regards conformation. An optically active molecule may be adsorbed on the one face and not on the other, and it is theoretically possible that the presence of an active substance may cause a holosymmetrical crystal to appear holoaxial in the development of either its faces or its etch-figures.

If this very interesting conclusion is verified by further investigation (the attempt to reverse the figures by using amyl alcohol of opposite rotatory power has not yet been made), it casts light on a puzzling problem. Crystallographers have, for instance, assigned potassium chloride, ammonium chloride, cuprous oxide, and barium, strontium, and lead nitrates to holoaxial classes. These crystals do not rotate the plane of polarisation of light, and in each case *X*-ray analysis assigns a structure of higher symmetry (cubic holohedral to the first three, pyritohedral to the last three). A similar explanation would apply to all these cases, a trace of optically active contamination determining the development of an apparently holoaxial form. It may be necessary to investigate anew many cases where a low type of symmetry has been assigned to a crystal on the evidence of rare forms.

The Interpretation of Rotation Photographs.

The rotating crystal method of Rinne, Schiebold, and Pólányi is becoming increasingly prominent as a convenient and powerful method of determining the space-group of a crystal. A mono-

[2] *Z. Physik*, 1926, **39**, 69; **A.**, 1085.

chromatic beam of *X*-rays falls on a crystal which is rotated about an axis perpendicular to the beam and the reflexions are received on a photographic plate, or on a cylindrical film centred about the axis of rotation. The crystal may be turned through a limited arc, or be completely rotated during the exposure. It is desirable to use a single crystal which is as perfect as possible, but very small specimens a fraction of a cubic mm. in volume suffice. The method lends itself readily to a measurement of the cell-dimensions, and the large number of reflexions which are recorded provides ample material for the determination of the space-group. The principal difficulty encountered is that of assigning indices to the spots on the plate or film, and some care must be exercised in doing this in order that trustworthy results may be obtained.

Methods of analysing the photographs have been described by Schiebold.[3] Recently an exhaustive discussion of the geometrical problem has been published by J. B. Bernal.[4] This is the first account in English which has appeared, and the care with which the author has prepared it will be widely appreciated. The examination of crystals with all types of symmetry is described, and numerous formulæ are given.

The array of formulæ appears somewhat forbidding at a first glance, but the nature of the problem must be borne in mind. In treatises on crystallography considerable space must be devoted to the description of methods of assigning a crystal to one of the 32 classes and of measuring its axial ratios with the goniometer, although experience has led to a choice of the most direct methods. Here the geometrical problem is of the simplest, a goniometer being used to measure the angles between faces by observing reflexions of a light-signal. In *X*-ray analysis, a far more complex problem presents itself. Reflexion takes place at all possible planes within the crystal, at angles depending on the spacing of the planes and the wave-length used. The very complicated record on plate or film contains enough information to make possible the choice between the 230 space-groups, and to give the dimensions of the unit cell. It is therefore not surprising that the technique of investigation is lengthy to describe and requires some apprenticeship in practice. No doubt experience will indicate ways of shortening the work, as has happened in the older and much simpler science of goniometrical measurement. Several such ways are described in Bernal's paper.

The Dynamics of the Crystal Lattice.

Some of the most interesting work on crystal structure which has

[3] *Z. Physik*, 1924, **28**, 355. [4] *Proc. Roy. Soc.*, 1926, [*A*], **113**, 117.

appeared in the last two or three years is concerned with the dynamics of the crystal lattice. The pioneer in this field was Max Born, and his classical treatment is surveyed in his monograph " Atomtheorie des festen Zustandes." Its application is as yet confined to crystal structures which may be regarded as composed of ions,* for practically nothing is known about the forces between neutral atoms united by bonds of other types. In the case of the crystals composed of ions, however, simple assumptions about the interatomic forces lead to a highly interesting explanation of many crystal properties. As this subject has not been dealt with recently in these Reports, a brief summary may be of interest.

In the absence of external forces distorting its structure, an ion is supposed to be isotropic or spherically symmetrical. When two ions are in proximity, the following forces exist :

1. An attraction or repulsion between the ionic charges.
2. An intrinsic repulsive force, dependent on the electronic configurations of the ions, which is inappreciable at large distances but rapidly rises to a high value as the ions approach one another.
3. Forces due to the polarisation of the ions in each other's electric fields.

The electrostatic forces of the first type obey Coulomb's law, and depend on the ionic charges and the distance between ionic centres. The intrinsic repulsive forces act independently of ionic charge, and are of the same nature as those which come into play, for instance, when two atoms of an inert gas rebound from each other in a gaseous collision. Born attempted to give these forces a formal expression by defining the potential energy of two ions at a distance r apart as being b/r^n. As is well known, Born deduced the index n for the ions in crystals of the sodium chloride type from the volume-elasticities of the crystals, for the compressibility of the crystal depends on the rate at which the intrinsic repulsive force increases as the ions are forced together. The index n was shown to have a value of about 9. Values for b were assumed such that attractive and repulsive forces in the crystals balanced each other. The heats of formation of the crystals from dispersed ions were then calculated, work being done by the electrostatic forces and against the repulsive forces as the ions came together. Born has devised an ingenious series of checks which show that these theoretical values are in good agreement with observation.

* The examination of the equilibrium conditions in crystalline argon (F. Simon and C. von Simson, *Z. Physik*, 1924, **25**, 160; *A.*, 1924, ii, 586; J. E. Lennard-Jones and P. A. Taylor, *Proc. Roy. Soc.*, 1925, [*A*], **109**, 476; **A.**, 1926, 11) is an exception to the above statement.

A further step was taken by Born and W. Heisenberg [5] in calculating the effect of ionic polarisation. In a symmetrical crystal such as that of sodium chloride, where every ion is surrounded by neighbouring ions, polarisation does not take place. If the salt is sublimed, and the ions dispersed as molecules of sodium chloride, each ion is strongly polarised by its partner. In any calculation of energy changes where ions are distorted, this polarisation must be taken into account. The response of the ion to an external field is expressed by a constant α, the ion acquiring an electrical moment αE in a field of strength E. Born deduces values of α from optical constants.

We may summarise by saying that the lattice theory in its simple form assigns to the ions constants Z, n, b, and α. Z measures the ionic charge Ze and α the " polarisability " of an ion. The constants b and n determine the potential energy b/r^n due to the intrinsic repulsive forces between a given pair of ions. Ionic models defined by these constants can be used in an examination of the following crystalline properties :

Energy of crystal lattice.
Surface energy of crystal face.
Dimensions and axial ratios of crystal lattice.
Elastic constants and strength of crystal.
Characteristic frequencies of the lattice.
Characteristic vibrations of groups such as CO_3'', SO_4''.
Piezo-electric effect.
Relative stability of alternative crystalline forms.
Refractive indices.
Optical activity.

Born's calculation [6] of the latent heats of sublimation of the alkali halides is a good example of the application of these conceptions. The potential energy U which is lost when a system of dispersed ions $Na^{\cdot}$ and Cl' comes together to form a crystal can be calculated. Starting with the same system of dispersed ions, the energy V can be calculated which is lost when the ions come together in pairs to form molecules. The heat of sublimation S, when the solid crystal passes into gaseous molecules, can be measured, and the three quantities should be connected by the equation $U - S = V$. The following table shows the extent to which the relation is satisfied, all energies being expressed in kg.-cals. per g.-mol.

	U.	S.	$U - S$.	V.	(V_0).
NaF	222	56·6	165	161	(147)
NaCl	182	44·3	138	139	(121)
NaBr	172	38·6	133	133	(114)
NaI	158	37·0	121	126	(105)

[5] *Z. Physik*, 1924, 23, 388; *A.*, 1924, ii, 434. [6] *Loc. cit.*

The quantities (V_0) have been calculated without allowance for the mutual polarisation of the ions in a molecule, which has been made in calculating V, and it will be seen that V is much closer to $U - S$ than V_0. Similar agreement is obtained for the remainder of the alkali halides.

A further and fundamental advance has been made by J. E. Lennard-Jones,[7] who has linked up the intrinsic repulsive forces between ions with the corresponding forces between atoms of the inert gases of similar electronic configurations. Lennard-Jones finds, in the first place, that the equations of state, thermal conductivities, and viscosities of the inert gases can be explained by inverse-power laws of the form λr^{-n} with suitable constants. In order to express the intrinsic force, n must be given values of 9, 10, or 11. The van der Waals attractive force is also important in the gaseous state and a corresponding term must be added, but it is so weak in comparison with the electrostatic forces between ions in crystals that it may be neglected in this case. In order to connect the forces between ions with those between inert-gas atoms, further assumptions must be made. For instance, the index n for two argon-like ions $K^{\cdot}$ and Cl' is supposed to be the same as that for argon itself. The force constant λ_1 between two similar ions is given by the equation $\lambda_1 = x^{n-1}\lambda_0$, where x represents the ratio of the dimensions of the ion to those of the inert-gas atom with a constant λ_0. Similar assumptions enable the force constants between unlike ions to be calculated. The ratios of the dimensions are based on considerations of refractivity (due originally to Wasastjerna) and atomic theory.

Starting with kinetic-theory data, Lennard-Jones has calculated the length of unit-cell edge for crystals of the sodium chloride and calcium oxide type, obtaining general agreement within 1 or 2% of the observed values. This is in itself a very striking achievement, and has recently been followed by a more elaborate analysis. Crystals of the calcite type referred to the customary axes are characterised by a rhombohedral angle which lies between 101° 55′ ($CaCO_3$) and 103° 28′ ($ZnCO_3$). The form of the crystalline structure is the result of equilibrium between forces of attraction and repulsion. W. L. Bragg and S. Chapman [8] attempted to calculate the rhombohedral angle theoretically by applying the principle of virtual work to small deformations of the structure, using a method

[7] *Proc. Roy. Soc.*, 1925, [*A*], **109**, 584; **A.**, 1926, 11; J. E. Lennard-Jones and (Miss) B. M. Dent, *ibid.*, 1926, [*A*], **112**, 231; **A.**, 888. These papers give further references to the work of these authors.

[8] *Ibid.*, 1924, [*A*], **106**, 369; *A.*, 1925, ii, 92; compare *Ann. Report*, 1924, **21**, 228.

which made it possible to obtain an approximate result without knowing the intrinsic repulsive forces. J. E. Lennard-Jones and (Miss) B. M. Dent,[9] and J. Topping and S. Chapman [10] have extended the investigation and taken into account the repulsive forces. A value for the effective distance between carbon and oxygen atoms must be assumed, since the nature of the bond is unknown. Lennard-Jones has shown that the sizes and shapes of the unit cell for all the carbonates can be explained by a distance of 1·08 Å. between the carbon and oxygen of a CO_3 group. Conformations of equal potential energy form contour lines in a graph where ordinate and abscissa define the shape and size of the unit cell, and these contour lines surround a point of minimum potential energy which corresponds to the conformation of equilibrium. A comparison for magnesium and calcium carbonates is given below.

	$MgCO_3$.		$CaCO_3$.	
	(Calc.).	(Obs.).	(Calc.).	(Obs.).
Rhombohedral angle	102° 24′	103° 21′	102° 18′	101° 55′
Distance between C-atoms	4·66	4·61	4·96	4·96

Thus the density and shape of the calcite crystal have been calculated from measurements of thermal conductivity and viscosity of neon and argon.

It is interesting to compare measurements of the CO_3 group made in very different ways. *X*-Ray measurements probably define the distance of the inner electrons surrounding the oxygen nucleus from the carbon nucleus, and give values between 1·24 Å. and 1·34 Å.[11] The double refraction of calcite [12] is accounted for by a distance of 1·27 Å. from carbon to an isotropic polarisable O″ ion. The form of calcite is explained by Lennard-Jones on the assumption of a distance of 1·08 Å., as defining the mean centre from which the electrostatic and repulsive forces act. Another line of attack is provided by the characteristic vibrations of the CO_3 group, but this has so far met with little success. It is well known that ions such as CO_3'' and SO_4'' are associated with definite frequencies in the infra-red region characteristic of the groups in crystals and in solutions. H. Kornfeld,[13] S. Chapman and A. E. Ludlam,[14] and P. A. Taylor [15] have tried to account for the infra-red frequencies

[9] *Proc. Roy. Soc.*, 1927, [*A*], **113**, 673, 690.
[10] *Ibid.*, p. 658.
[11] (Sir) W. H. Bragg, *Phil. Trans.*, 1915, [*A*], **215**, 253; R. W. G. Wyckoff, *Amer. J. Sci.*, 1920, **50**, 317.
[12] W. L. Bragg, *Proc. Roy. Soc.*, 1924, [*A*], **106**, 346; *A.*, 1925, ii, 92.
[13] *Z. Physik*, 1924, **26**, 205; *A.*, 1925, ii, 12.
[14] *Phil. Mag.*, 1925, [vi], **50**, 822; *A.*, 1925, ii, 1025.
[15] *Ibid.*, p. 1158; *A.*, 1925, ii, 1115.

due to oscillations of atoms in the CO_3 group, but the attempts have led to paradoxical results, and it seems that we do not yet know enough about the interatomic forces within the group.

Certain papers by F. Hund [16] are of great interest. The majority of diatomic compounds crystallise in three typical forms. In the cæsium chloride type, ions of one kind occupy cube corners and those of the other kind cube centres, each ion having eight neighbours of opposite sign. In the sodium chloride type the corresponding number is six, and in the zinc sulphide type four. Hund calculates the heat of formation of the three types for different inverse-power laws of repulsion in order to determine which is the most stable form. He shows that, *ceteris paribus*, when $n>35$ it is the cæsium chloride type, when $35>n>6$ it is the sodium chloride type, and for smaller values of n the zinc sulphide type. Similar conclusions are reached as to the criteria which differentiate between the alternative forms typified by CaF_2, TiO_2, Cu_2O. The author further shows that the polarisability is a highly important factor in determining the type of crystal. Ions which are easily polarised are more likely to set as "molecular crystals" than as "ionic crystals" (Koordinationsgitter). If α is large, a symmetrical lattice is not the most stable form, since potential energy is further reduced by a one-sided deformation of pairs of ions. As an intermediate stage between symmetrical crystals like sodium chloride, on the one hand, and groups of molecules, on the other, there are the very interesting layer crystals (Schichtengitter). In cadmium iodide and zirconium sulphide, co-ordination takes place in sheets of symmetrically-placed positive and negative ions, but these sheets are separated from each other as definitely as distinct molecules would be. The molecule has indefinite extension in two directions only, as compared with three in sodium chloride. Hund discusses the limiting values of α for which these layer-crystals become the type of greatest stability.

The results are suggestive as indications of the dependence of crystalline form on ionic properties, but it is doubtful whether sufficient is known about the intrinsic repulsive forces to make possible the application of so delicate a test, particularly when it is remembered that change of temperature (a factor not taken into account in the calculations) often causes one form to change to another. The most uncertain feature of all these examinations into crystalline dynamics would appear to be the assumptions made about the intrinsic repulsive forces. The constants of an inverse-power law can be adjusted so as to explain lattice-spacings and

[16] *Z. Physik*, 1925, **34**, 833; *Physikal. Z.*, 1925, **26**, 682; *A.*, 1925, ii, 1132.

crystal-compressibilities, but it does not follow that the same law will hold true over other ranges of interatomic distance. In calculations of crystal energy such as those made by Born, this does not matter greatly, for the work done against the repulsive forces only appears as a correction to the far greater work done by the electrostatic forces, and the adjusted inverse-power law will give a fair approximation to the most important part of the correction. In the calculation of crystalline axial ratios, and of the relative stability of different types, it is important to know the law of force over a wide range of distance, and the assumption of a simple inverse-power law may lead to very wrong conclusions. Lennard-Jones's deduction of the law from kinetic-theory data is less open to criticism because a wide range is here involved. A more complete understanding of the intrinsic repulsive forces, however, appears to be most desirable for further advance.

G. Heckmann [17] has worked out the constants of the diatomic crystals (NaCl, CsCl, and ZnS types), taking into account, not only the electrostatic and intrinsic repulsive forces, but also the forces due to polarisation of the ions. He shows what modifications are to be introduced into the usual formulæ of Born for the dielectric constants, piezo-electric constants, and wave-lengths of the "Reststrahlen." The only elastic constants not affected by the new theory are Young's modulus, the modulus of rigidity, and the coefficient of compressibility. The calculation of the surface energy of crystals is important because of its bearing on the forces operative at interfaces in chemical action. Born [18] has made calculations of the quantity. J. E. Lennard-Jones and P. A. Taylor [19] recalculated the values with improved values for the constants determining the repulsive forces, and recently J. Biemüller [20] has considered the effect of polarisation of the ions. He shows that this may lower the value of the surface energy by as much as 40% in extreme cases, although the correction may in other cases be only a few units %.

A paper by H. G. Grimm and A. Sommerfeld [21] raises an interesting point concerning the relation between chemical bonds and crystalline structure. The authors ascribe the tetrahedral type of structure (ZnS, BeO, AlN) to a tendency on the part of the atoms towards a completed four-electron shell, analogous to the well-known tendency towards a 2-shell, 8-shell, and 18-shell. They point out the similarity between these structures and the diamond structure. To quote from a recent lecture by Sommerfeld "Tetrahedral

[17] *Z. Physik*, 1925, **31**, 219; *Z. Krist.*, 1925, **61**, 250.
[18] "Atomtheorie des festen Zustandes," p. 743.
[19] *Proc. Roy. Soc.*, 1925, [*A*], **109**, 496; **A.**, 1926, 11.
[20] *Z. Physik*, 1926, **38**, 759; **A.**, 1086. [21] *Ibid.*, **36**, 36; **A.**, 560.

structure is only found in those binary compounds in which both partners are equidistant and at most four places from a 4-shell; that is, from the elements C, Si, Ge, Sn, Pb." Hund, as has been mentioned above, ascribes the formation of these compounds to a low index n for the repulsive forces (" soft " atoms), but the possibility of its being due to a totally different type of bond must be borne in mind.

The Intensity of X-Ray Reflexion.

Progress towards a more complete understanding of the arrangement of the atoms in crystals is dependent on a knowledge of the laws which govern X-ray diffraction. In seeking to extend the powers of X-ray analysis, we are confronted with a problem which is very like that of improving the resolving power of an optical instrument. When the possibilities of analysis were first realised, the most general application of the principles of interference sufficed for the simple structures that were then attempted, but greater precision is needed when complex structures are under examination. In an X-ray examination, the waves scattered by the crystal unit in different directions are measured by an ionisation chamber or photographic plate, and from their recorded strength an image of the scattering object is built up step by step. A resolving power which will reveal at once the coarse " black and white " of the rock-salt structure is powerless to deal with the faint half-tone shades which outline the organic molecule.

Recently P. P. Ewald [22] directed attention to the erroneous assumptions often made in crystal analysis—in particular, to the assumption that intensity of reflexion is proportional to the square of the " structure factor." A paper by W. L. Bragg, C. G. Darwin, and R. W. James [23] reviews the subject of " Intensity of Reflexion." The difficulties of precise analysis arise in the theoretical interpretation of the results of experiment, and not in the quantitative measurements, which can easily be made with sufficient accuracy. In the first place, it is necessary to know the laws which govern the scattering of X-rays in different directions by the individual atom. This will depend on the electronic configuration of the atom, for interference between waves scattered by the electrons in the atom will take place. The scattering depends on the heat-motions of the atoms, which cause a diminution of scattering power as the temperature rises. It is probable that the Compton effect plays a large part, for much of the radiation which is scattered is altered in wavelength and therefore is not included in the regularly-diffracted beam.

[22] *Physikal. Z.*, 1925, **26**, 29.
[23] *Phil. Mag.*, 1926, [vii], **1**, 897; **A.**, 663.

There is evidence, which will be discussed below, of a reversal of phase when long waves are scattered by inner electrons belonging to atoms of high atomic weight. These factors all influence the amount of radiation scattered by an atom. The combination of the waves from these atoms to form a wave scattered by the structural unit as a whole, and the further combination to form the wave reflected by a homogeneous fragment of crystal, all appear to be governed by the classical laws of interference, and to lend themselves to exact analysis. Difficulties arise again, however, when we attempt to apply a theory of intensity of reflexion to actual crystal-structures.

The intensity of reflexion may be calculated on the supposition that a crystal is absolutely perfect, plane succeeding plane with mathematical regularity. Given the atomic arrangement, and hence the amount of radiation scattered by each unit of structure, a formula can be deduced for the total radiation reflected as a crystal is rotated through the reflecting position (this is a convenient way of defining reflecting power). On the other hand, a crystal may be regarded as a mosaic of minute crystalline fragments, each perfect in itself but irregularly joined to its neighbours. On this assumption, a second formula for reflecting power can be deduced which is quite different from the first. The two formulæ were first worked out by Darwin in 1914, but the importance of the formula for the perfect crystal was not properly realised until Ewald arrived at the same formula independently many years afterwards. The reflecting power calculated by the second formula may be 10—50 times as great as that for a perfect crystal, the apparent paradox of a greater reflecting power for the imperfect crystal being explained by the larger range of angles over which it reflects.

The most important difference between the two formulæ lies in their dependence on "Structure Factor." It is customary to denote by the symbol F the power of the structural unit to scatter X-rays in a given direction, expressed in terms of the radiation scattered by a single electron, so that F is a numerical ratio which is a dimensionless function of angle of scattering, wave-length, and atomic dimensions. The perfect crystal reflects X-rays completely over a short range of angles which is proportional to F, so that F appears in the first power in the expression for reflecting power. The imperfect crystal reflects a weaker beam over a wide range of angle, the integrated reflexion being proportional to F^2. It is, of course, essential to know which formula should be used in any given case. In general, it would appear that actual crystals tend to be of the mosaic type, but are too perfect for it to be possible to apply the "imperfect crystal" formula without correction. The correc-

tions take the form of allowances for "primary extinction" and "secondary extinction" initiated by Darwin. A mathematical discussion of the reflecting power in intermediate cases between the large perfect crystal and the small, homogeneous fragment is given by I. Waller.[24]

The final results of quantitative analysis, when corrections for extinction have been successfully applied or have been rendered unnecessary by the use of the powder method, can be expressed as a series of measurements of the scattering coefficient F. These values of F represent the data by the aid of which the image of the scattering unit must be formed. Two courses may be followed, and it is interesting to trace the relation between them. The usual course consists in making assumptions about the scattering powers of the individual atoms, and testing various models by comparing the values of F calculated for them with those actually observed. Recently W. Duane [25] has proposed a very simple way of inverting this process. He shows that the values of F are the coefficients in a Fourier series which represents the spatial distribution of scattering matter in the crystal structure. Series can be formulated which give the density of scattering matter at a point, its radial distribution around an atomic centre, or its distribution in sheets parallel to a given crystal plane. R. J. Havighurst [26] has applied Duane's formula to experimental measurements on rock-salt by Bragg, James, and Bosanquet, and has calculated the electron density along certain lines in the rock-salt crystal. The results are shown in Fig. 1. The four curves represent the density plotted as ordinate in passing (1) along a cube edge through alternate atoms of chlorine and sodium, (2) along the cube diagonal, (3) along a face diagonal through atoms of chlorine alone, and (4) along a diagonal through atoms of sodium alone. The directness of the method is a very attractive feature. No assumptions about atomic positions or scattering power are made, the experimental results being directly applied to a determination of the distribution of scattering matter, which may in its turn be interpreted as due to the atomic arrangement.

The new method has its limitations. X-Ray analysis measures the coefficients F of the terms of the Fourier series, but not their phases, which must be deduced from considerations of symmetry and of probable crystalline arrangement. Further, the number of terms in the series which can be measured is limited by the number of spectra yielded by the crystal, and the series often converges

[24] *Ann. Physik*, 1926, **79**, 261.
[25] *Proc. Nat. Acad. Sci.*, 1925, **11**, 489.
[26] *Ibid.*, p. 502; 1926, **12**, 380; **A.**, 780.

slowly. The absence of higher terms from the series when summed may give a very erroneous idea of electron distribution, just as a microscope of low resolving power may add false detail to an image. Nevertheless, the method has very great possibilities and will no

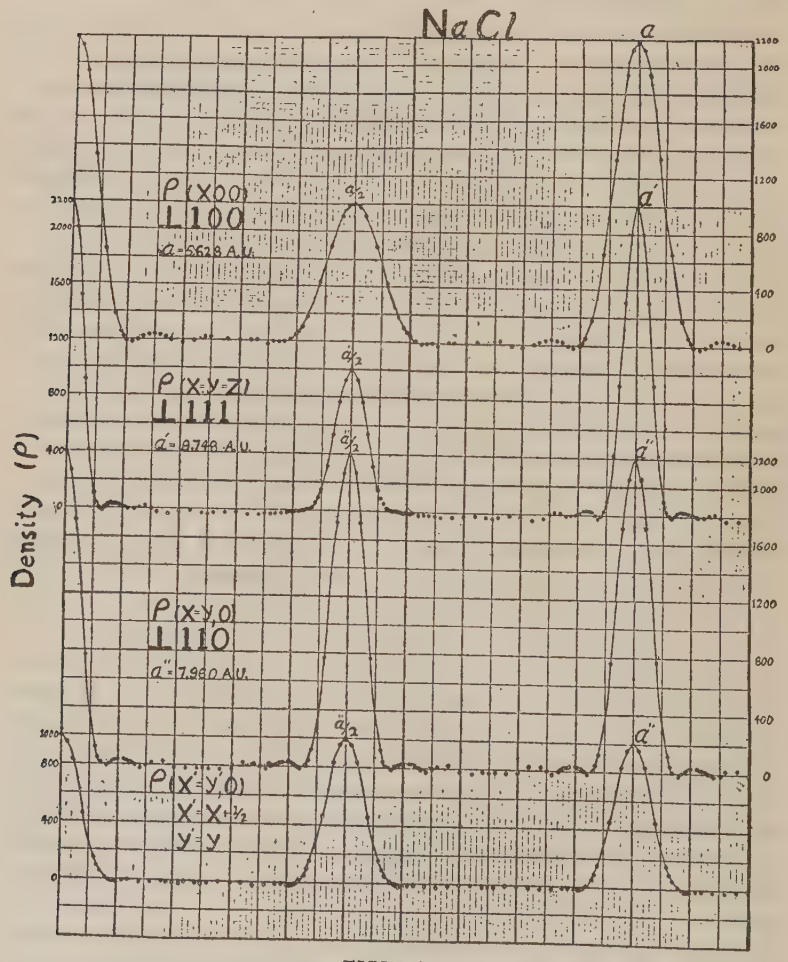


FIGURE 1

doubt be widely used in future analysis. Its application to the complex crystal beryl [27] and to the mercurous halides [28] shows how it can be used for direct determination of parameters. Duane's work is based on a quantum theory of diffraction, but A. H.

[27] W. L. Bragg and J. West, *Proc. Roy. Soc.*, 1926, [*A*], **111**, 691; **A.**, 889.
[28] R. J. Havighurst, *J. Amer. Chem. Soc.*, 1926, **48**, 2113; **A.**, 995.

Compton [29] has shown that the classical theory of diffraction leads to an exactly similar expression. Since the Fourier analysis yields the average distribution of scattering matter directly, it would appear to be the best way of detecting asymmetry of the atom in the crystalline structure. It is one of the most interesting additions to the technique of X-ray analysis of recent years.

The temperature factor has been the subject of a theoretical study by I. Waller.[30] Debye originally proposed an expression e^{-M} for the temperature factor of a cubic crystal, in which

$$M = \frac{6h^2}{\mu k\theta} \cdot \frac{\sin^2\theta}{\lambda^2} \cdot \frac{\varphi(x)}{x}$$

$$\text{where } x = \frac{\text{Characteristic temperature } \Theta \text{ of crystal}}{\text{Actual temperature } T}.$$

Waller has deduced that the temperature factor should be e^{-2M}, not e^{-M}. R. W. James [31] has measured the factor for rock-salt between temperatures of 90° and 900° K. He has proved that M varies with $\sin^2\theta/\lambda^2$ to a high degree of accuracy by using different faces as reflectors, and has shown that Waller's formula (not Debye's) is closely obeyed between 90° and 600° K. Beyond this temperature, the intensity of reflexion falls away more quickly than is indicated by theory, presumably owing to a change in the elastic constants of the crystal. These measurements of temperature factor are interesting because they yield a direct estimate of the amplitude of vibration of the atoms in the crystal.

The F-curves of individual atoms can be obtained from the study of simple crystals, and trustworthy measurements are accumulating. R. W. James and J. T. Randall [32] have measured the scattering powers of calcium and fluorine in calcium fluoride. R. J. Havighurst [33] has published curves for calcium, fluorine, lithium, and sodium, working with lithium, sodium, and calcium fluorides. A. Claassen [34] has obtained values for iron and oxygen in Fe_3O_4. Havighurst's measurements are especially interesting because they were made with crystalline powders, so that secondary extinction was absent. By grinding the powder to very fine dimensions, Havighurst tried to avoid primary extinction. His results with the finest powders are in close agreement with each other and with those

[29] *Physical Rev.*, 1926, **27**, 510.

[30] *Z. Physik*, 1923, **17**, 398; "Theoretische Studien zur Interferenz u. Dispersionstheorie der Röntgenstrahlen," Uppsala Universitets Arsskrift, 1925.

[31] *Proc. Manchester Lit. Phil. Soc.*, 1926, **71**.

[32] *Phil. Mag.*, 1926, [vii], **1**, 1202; **A.**, 663.

[33] *Proc. Nat. Acad. Sci.*, 1926, **12**, 380; **A.**, 780.

[34] *Proc. Physical Soc.*, 1926, **38**, 482; **A.**, 1072.

of Bragg, James, and Bosanquet for large rock-salt crystals after making allowance for secondary extinction. An accurate determination of the F-curve is interesting, because it gives evidence as to the distribution of electrons in the atom. Bragg, James, and Bosanquet used a " trial and error " method of finding electronic distribution which explained the F-curves. R. J. Havighurst [35] and A. H. Compton [36] have applied the Fourier analysis to the same problem. The electron-distribution curves of Compton are similar to those obtained by Bragg, James, and Bosanquet and by Havighurst from the same data, but show more detail. The radial distribution falls to zero at about 1·1 Å. from the centre of the sodium ion, and 2·0 Å. from the centre of the chlorine ion. Compton finds interesting peaks in the radial distribution curves which he attributes to the orbital extremities of different electronic groups in the crystal.

In deducing electronic configurations, however, the possible influence of the Compton effect must be borne in mind, for it may vitiate conclusions drawn by using the classical laws of interference. H. Kallmann and H. Mark [37] examined the possible interference of the modified radiation, which Compton has shown to be scattered with a change of wave-length and explained by a quantum hypothesis. E. J. Williams [38] has discussed the influence of the Compton effect on the F-curve. It is assumed (1) that only the unmodified radiation contributes to reflexion, and (2) that Compton's criterion for modification (as developed by Jauncey) holds, *viz.*, that if the deflexion of the scattered quantum gives sufficient energy to the scattering electron to eject it from the atom, the ray is modified. Otherwise the quantum is scattered without change of wave-length. Williams applies this criterion to atomic models for calcium and fluorine calculated by Hartree. The F-curve, allowing for the Compton effect, falls more steeply than the classical curve due to Hartree, and is smoother in outline. In fact, it approximates much more closely to the observed F-curve. The work of Williams and Jauncey may lead to a satisfactory agreement between theory and experiment, which has hitherto been unobtainable.

A fundamental point is raised by H. Mark and L. Szilard.[39] Rubidium bromide (111) planes consist of alternate sheets of rubidium and bromine atoms. These atoms are so nearly alike in scattering power that (111) and (333) reflexions, for which the atoms are in opposition, are in general too weak to be observed. If,

[35] *Proc. Nat. Acad. Sci.*, 1925, **11**, 506.
[36] *Loc. cit.*
[37] *Z. Physik*, 1926, **36**, 120; **A.**, 551.
[38] *Phil. Mag.*, 1926, [vii], **2**, 657; **A.**, 988.
[39] *Z. Physik*, 1925, **33**, 688.

however, a wave-length *between the* Rb *and* Br *K-absorption edges* is used, the reflexions appear (Sr K_α-radiation fulfils this condition). The K-electrons alone can be concerned in the effect, and the positive result obtained by Mark and Szilard means that the scattered waves from these electrons in rubidium and bromine differ in amplitude or phase. A difference in phase would correspond to the difference in phase on the classical theory of the response of an oscillator to forced vibrations of higher or lower frequency. It may be necessary to give a negative sign to the contributions to the F-curve from the K-electrons of atoms of high atomic weight.

The preceding discussions deal largely with atomic structure, but the points which are raised are of vital importance to crystal analysis. Refinement of technique is essential in order that X-ray methods may be used to the full in examining structure.

Inorganic Crystals.

Among the more interesting of the inorganic structures recently analysed are potassium and sodium trinitride.[40] Sodium trinitride, NaN_3, is rhombohedral with one molecule to the unit cell. The sodium atoms lie at the corners of the unit rhombohedron ($a = 5{\cdot}481$ Å., $\alpha = 38°\ 43'$). The three nitrogen atoms are collinear and lie along the diagonal of the rhomb, one atom at the centre of the cell, the others symmetrically on either side of it at a distance of 1·17 Å. Potassium trinitride, KN_3, forms tetragonal crystals, with four molecules to the unit cell ($a = 6{\cdot}094$ Å., $c = 7{\cdot}056$ Å). The N_3 group has the same form and dimensions as in sodium trinitride, but the lines of the groups are perpendicular to the tetragonal axes and at an angle of 45° to the cell edges. The difference in structure between the sodium and potassium salts is in all probability due to the much greater size of the potassium ion. Many similar cases occur; *e.g.*, sodium nitrate has a calcite structure whilst potassium nitrate is orthorhombic and similar to aragonite.

We may compare with the N_3 group the structures of solid nitrous oxide and solid carbon dioxide.[41] These compounds form cubic crystals with symmetry of the pyrites type. The groups N_2O and CO_2 are well marked and are linear, the atomic centres lying on the four non-intersecting trigonal axes. In nitrous oxide, the distance from nitrogen to oxygen is given as 1·15 Å., which indicates a close

[40] S. B. Hendricks and L. Pauling, *J. Amer. Chem. Soc.*, 1925, **47**, 2904; **A.**, 1926, 113.

[41] J. de Smedt and W. H. M. Keesom, *Proc. K. Akad. Wetensch. Amsterdam*, 1924, **27**, 839; *A.*, 1925, ii, 484; H. Mark and C. Pohland, *Z. Krist.*, 1925, **61**, 293; J. C. McClennan and J. O. Wilhelm, *Trans. Roy. Soc. Canada*, 1925, [iii], **19**, III, 51; **A.**, 1926, 13.

similarity between the groups N_2O and N_3. The length of the cube edge is 5·74 Å. For carbon dioxide Mark and Pohland give 5·62 Å. for the cube edge, and de Smedt and Keesom agree with this. McClennan and Wilhelm give 5·74 Å., but this is not in good agreement with the accepted value of the density of solid carbon dioxide at the temperature of liquid air. The three estimates of the distance C—O differ greatly, for Mark and Pohland give 1·59 Å., McClennan and Wilhelm 1·25 Å., and de Smedt and Keesom 1·05 Å. Evidently further investigation is needed. It is interesting to note that the distance N—N is of the same order as the distance N—O in the NO_3' group of sodium nitrate.

Further evidence of the existence of definite complex ionic groups having a form which is permanent from compound to compound is given by the analysis of several sulphates. Lithium potassium sulphate [42] (hexagonal), barium sulphate, strontium sulphate, lead sulphate,[43] and anhydrite, the anhydrous form of calcium sulphate,[44] have now been analysed. In all these compounds the SO_4 group has approximately the same size and form. The four oxygen atoms are arranged with their centres at the corners of a nearly regular tetrahedron whose edge is about 2·5 Å. and at whose centre the sulphur atom lies. The space occupied by the group in the different crystals can be accounted for by describing about the centres of the oxygen atoms spheres of radius 1·35 Å. The group can thus be considered as made up of four O^{-2} ions held together strongly by the S^{+6} ion at its centre. The distance S—O is about 1·55 Å. Barium, strontium, and lead sulphates are members of an interesting isomorphous series including among other compounds the perchlorates and permanganates of potassium, rubidium, cæsium, and ammonium. Measurements on potassium perchlorate and permanganate [45] show that the structures of these compounds are essentially similar to those of the sulphates and indicate that the XO_4 group has very much the same dimensions in all of them and is the determining factor in deciding the structure. The crystals of the barytes group are orthorhombic and the structure belongs to the space group V_h^{16}. Each metal ion is surrounded by twelve nearly equidistant oxygen neighbours belonging to the SO_4 groups.

Anhydrite, although also orthorhombic, belongs to the group V_h^{17}

[42] A. J. Bradley, *Phil. Mag.*, 1925, [vi], **49**, 1225; *A.*, 1925, ii, 638; compare *Ann. Report*, 1925, **22**, 253.

[43] R. W. James and W. A. Wood, *Proc. Roy. Soc.*, 1925, [*A*], **109**, 598; **A.**, 1926, 13.

[44] J. A. Wasastjerna, *Soc. Scient. Fennica*, 1925, **2**, 26; *Phil. Mag.*, 1926, [vii], **2**, 992; **A.**, 1195; E. C. S. Dickson and W. Binks, *ibid.*, p. 114; **A.**, 781.

[45] R. W. James and W. A. Wood, *loc. cit.*

and has a structure quite different from that of barium sulphate The crystal has two reflexion planes of symmetry on the intersection of which the sulphur atoms lie. The oxygen atoms form a tetrahedral group about the sulphur and lie in pairs on the symmetry planes. The calcium atoms lie on the intersections of the planes and alternate with the SO_4 groups. We have here an interesting case of two compounds, chemically closely akin, forming very different crystals, while compounds as distinct chemically as barium sulphate and potassium perchlorate form very similar crystals. There seems to be little doubt that the size of the ionic domain of the metal ion is the determining factor. $K^{\cdot}$ and $Ba^{\cdot\cdot}$ are similar in size, but $Ca^{\cdot\cdot}$ is considerably smaller, so that twelve oxygen ions can no longer pack round it.

The idea of a definite atomic or ionic domain must of course be applied with proper caution, but so much evidence that an approximately constant volume is occupied by an ion of a given type from crystal to crystal is now available that it would be foolish to ignore it altogether. By its aid it has been possible to attack some of the more complex inorganic structures of lower symmetry, where the atoms are fixed by a number of parameters. Most of these compounds contain oxygen, and a knowledge of the fact that the centres of two oxygen atoms do not as a rule approach closer to one another than about 2·7 Å., unless held by very strong forces, as in some of the complex ions, is of great use in selecting structures which are probable physically from those which are possible geometrically.

Good examples of this may be found in the analyses of a number of the gem-stones, which consist as a rule of oxygen in combination with ions such as $Be^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, $Si^{\cdot\cdot\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, and $Mg^{\cdot\cdot}$, all of which are small compared with the oxygen. The latter, therefore, appear frequently to be nearly close-packed either in cubic or hexagonal array, whilst the smaller ions are able to pack in the holes between the oxygens holding them together, but slightly distorting or expanding the close-packed structure and lowering its symmetry. Compounds whose dimensions indicate that they are essentially hexagonally close-packed oxygen ions are aluminium oxide,[46] beryllium oxide,[47] chrysoberyl, $BeAl_2O_4$,[48] and olivine.[49] The first two of these

[46] W. L. Bragg, *Proc. Roy. Soc.*, 1924, [*A*], **106**, 346; *A.*, 1925, ii, 92; S. B. Hendricks and L. Pauling, *J. Amer. Chem. Soc.*, 1925, **47**, 781; *A.*, 1925, ii, 368.

[47] L. W. McKeehan, *Proc. Nat. Acad. Sci.*, 1922, **8**, 270; *A.*, 1922, ii, 766; G. Aminoff, *Z. Krist.*, 1925, **62**, 113; **A.**, 1926, 227; W. Zachariasen, *Z. physikal. Chem.*, **1926, 119**, 201; **A.**, 562.

[48] W. L. Bragg and G. B. Brown, *Proc. Roy. Soc.*, 1926, [*A*], **110**, 34; **A.**, 227.

[49] *Idem, Z. Krist.*, **1926, 63**, 538; **A.**, 995.

crystals are hexagonal; the others are orthorhombic. In other cases, a local close-packing of oxygen ions occurs whilst there are considerable spaces elsewhere. An example of such a structure is beryl, $Be_3Al_2Si_6O_{18}$.[50] In this crystal, the silicon and oxygen atoms form rings of the composition Si_6O_{18}, built up by SiO_4 groups, each joined to its neighbour on either side by an oxygen atom held in common. The distance O—O in an SiO_4 group is 2·54 Å. This closer grouping may be compared with that in the group SO_4.

The crystalline forms of silica, *viz.*, quartz,[51] cristobalite,[52] and tridymite,[53] also show the grouping of oxygen atoms in tetrahedra about the silicon atoms. The recent analysis of tridymite by Gibbs extends the very striking relationship between the many modifications of silica. The distance O—O in the SiO_4 groups of these crystals is about 2·52 Å. Garnet, $Ca_3Al_2Si_3O_{12}$, has been analysed by G. Menzer,[54] and here again the distances between the oxygen atoms are everywhere about 2·7 Å.

In a series of papers, H. Ott [55] has investigated the structures of the four modifications of carborundum, SiC. In all these structures, the carbon atoms are surrounded tetrahedrally by four silicon atoms and *vice versa*, the distance from carbon to silicon being 1·90 Å. There are two simple ways of making an arrangement of this type—one, analogous to the structure of diamond, typified by the cubic zinc-blende lattice, the other typified by the hexagonal zinc sulphide, wurtzite. The so-called amorphous modification of carborundum has the simple zinc-blende lattice; the other modifications, however, are trigonal or hexagonal and show remarkable alternations of the zinc-blende and wurtzite lattices along the axes. Modification II is hexagonal, $a = 3{\cdot}09$ Å., $c = 15{\cdot}17$ Å., with 6 molecules to the cell. Modification I is trigonal, but expressed in hexagonal terms the unit cell has 15 molecules, $a = 3{\cdot}09$ Å., $c = 37{\cdot}9$ Å. Modification III is dihexagonal, $a = 3{\cdot}09$ Å., $c = 10{\cdot}09$ Å. No other simple compounds are known in which the dimensions of the elementary cell are so large. It might be expected that, with the two types of arrangement possible, twinning would take place very readily, but that the twinning should be so regular and on the small scale of the elementary cell is very remarkable.

[50] W. L. Bragg and J. West, *Proc. Roy. Soc.*, 1926, [*A*], **111**, 691; **A.**, 889.

[51] (Sir) W. H. Bragg and R. E. Gibbs, *ibid.*, 1925, [*A*], **109**, 405; **A.**, 1926, 13.

[52] R. W. G. Wyckoff, *Amer. J. Sci.*, 1925, **9**, 448; *A.*, 1925, ii, 638.

[53] R. E. Gibbs, *Proc. Roy. Soc.*, 1926, [*A*], **113**, 351.

[54] *Z. Krist.*, 1926, **63**, 157.

[55] *Ibid.*, 1925, **61**, 515; **62**, 201; **63**, 1; **A.**, 1926, 562.

V. M. Goldschmidt [55a] has prepared a most interesting and valuable summary of present knowledge about the structure of the simple inorganic compounds. In many cases, where a few members only of a series of crystals had been analysed, he and his collaborators have completed the examination of the series. This extensive survey has revealed interesting relationships between the structures of the compounds. The relationships are interpreted by considering two properties of the ions which build up two crystals as being of prime importance, their size and the extent to which they can be polarised. A broad treatment along these lines introduces law and order into the mass of information about inorganic structure, and it is striking to see what an immense number of compounds have structures which approximate to certain simple types. The summary covers so wide a field that it is difficult to select any of the special points in it for mention; a study of it should be made by anyone who is interested in chemical crystallography.

Interesting work on the structure of metals and alloys has been done during the year. The discussion of this is reserved for a future Report, both on account of lack of space and because the researches in general have not reached that stage of completion which is desirable for a Report.

Organic Crystals.

Cellulose.—Readers of last year's Annual Report who are interested in the *X*-ray investigation of cellulose will find it profitable to consult a recent communication by R. O. Herzog.[56] This is a discussion of all the experimental data that are as yet available, and is the most complete account in English that has appeared hitherto.

Rubber.—In the same connexion must be mentioned also the important work of E. A. Hauser and H. Mark [57] on the structure of rubber. These authors have investigated in detail the phenomenon, discovered by J. R. Katz, [58] that rubber when stretched develops a strongly-marked crystalline structure, which disappears on heating, or on releasing the tension. In the unstretched state, the structure is apparently amorphous, but on extension rubber gives rise to an *X*-ray photograph similar to that usually obtained from asbestos, *i.e.*, it develops a structure made up of crystallites which are all oriented so that a certain crystallographic axis always

[55a] "Geochemische Verteilungsgesetze der Elemente VII. Die Gesetze der Krystallochemie," *Norske Videnskaps-Akademi I*, Mat. Nat. Kl., 1926, No. 2.

[56] *J. Physical Chem.*, 1926, **30**, 457; **A.**, 677.

[57] *Koll. Chem. Beih.*, 1926, **23**, 64; **A.**, 1098; Ambronn Festschrift, 1926, 63.

[58] *Kolloid-Z.*, 1925, **36**, 300; **37**, 19; *A.*, 1925, ii, 667, 969.

points along the direction of tension.[59] As the extension is increased, the positions of the spots on the photograph remain unaltered, but their intensity increases to a degree nearly proportional to the extension, whilst the intensity of the "amorphous" ring decreases in a similar manner. A careful examination of the photographs has furthermore shown that the amount of crystalline phase is increased, *not* by the growth of old crystallites, but by the continuous formation of new crystallites. A possible crystal unit has been deduced which contains four C_5H_8-groups. This important result shows that the molecular weight is relatively small—an observation similar to the one already made on the crystallites of cellulose. In the papers mentioned, the physical properties of rubber are discussed in connexion with these striking results.

Long-chain Compounds.—*X*-Ray investigation of these compounds continues to yield new and interesting results. The latest paper [60] on the subject deals with a phenomenon previously observed by Müller in the hydrocarbons, *viz.*, the existence of two or more crystal forms. Piper, Malkin, and Austin have examined this polymorphism in greater detail. They have observed three types of *X*-ray spectra for the higher fatty acids, besides recording various irregularities in spacing associated apparently with different modes of preparation and mounting. The authors do not appear to be justified in interpreting their observations as indicating the existence of at least two forms of chain. Until the space-group and complete structure of the crystals have been worked out, nothing further can be concluded than that they are capable of existing in polymorphous forms, as happens in the case of so many other crystals. An exceedingly interesting point deserves mention, *viz.*, that mixtures of stearic and palmitic acids show *only one* long spacing which is continuously variable with the composition of the mixtures, after the manner of ordinary isomorphous mixtures, even though there is more than 4 Å. difference between the normal lengths of the two chains.

i-*Erythritol.*—This compound has been shown [61] to be based on the space-group C_{4h}^6 of the tetragonal-bipyramidal class. The body-centred cell contains eight molecules, each being symmetrical about either a centre or a dyad axis of symmetry. But, in agreement with the conclusions of stereochemistry, the crystal evidence is strongly in favour of a centro-symmetrical molecule.

Tervalent Metallic Acetylacetones.[62]—From *X*-ray examination of

[59] Compare *Ann. Report*, 1925, **22**, 247.
[60] S. H. Piper, T. Malkin, and H. E. Austin, *J.*, 1926, 2310; **A.**, 1083.
[61] W. G. Burgers, *Phil. Mag.*, 1926, [vii], **1**, 289; **A.**, 339.
[62] W. T. Astbury, *Proc. Roy. Soc.*, 1926, [*A*], **112**, 448; **A.**, 996.

a series of ten of these compounds, the nature of the remarkable isotrimorphism which they collectively exhibit has been elucidated. The α-(monoclinic) form, space-group C_{2h}^5, and the β-(orthorhombic) form, space-group C_{2v}^7, each contain four chemical molecules, whilst the γ-(orthorhombic) form, space-group C_{2v}^9, contains sixteen molecules, and must therefore be assumed to be built up of associated groups of four molecules each. The molecular distribution in all three cases is similar, the difference lying in the respective molecular orientations. Although the molecules in all three cases are crystallographically asymmetric, there is little doubt that the atomic configuration known to stereochemistry holds in all three structures. All three forms are racemates.

Basic Beryllium Acetate and its Homologues.[63]—Laue photographs of basic beryllium acetate have shown that its space-group is T_h, and that, consequently, its molecular symmetry is only twelvefold, namely, four triad axes and three dyad axes. Even this lower type of symmetry is more than would be expected unless we neglect the hydrogens of the methyl groups. Their effect on the crystal symmetry must be inappreciable, otherwise it would be difficult to explain the dyad axes which the methyl groups undoubtedly possess. A similar molecular distribution prevails in the basic pivalate, but in this compound (monoclinic domatic, space-group C_s^4) the substituted methyl groups assert themselves and the molecular symmetry is completely lost. Certain observations have been made also on the basic butyrates which point to asymmetric molecules, as is to be expected.

The writer wishes to acknowledge his indebtedness to Dr. J. E. Lennard-Jones, Dr. A. Westgren, Mr. W. T. Astbury, and Mr. R. W. James for assistance in the preparation of the Report.

W. L. Bragg.

[63] G. T. Morgan and W. T. Astbury, *ibid.*, p. 441; A., 995.

SUB-ATOMIC PHENOMENA AND RADIOACTIVITY.

The two years (1925—6) under review may possibly be considered somewhat disappointing as far as actual advance in nuclear physics is concerned. In radioactivity itself, the most interesting problems, such as the mechanism of disintegration and the origin of actinium, still appear too difficult of direct access, although the work of analysis of β-ray spectra and the more accurate fixing of constants, so necessary in the preparation for further advance, is well maintained. In two other important fields, the disintegration of nuclei by the impact of α-rays, and the measurements of nuclear masses by the mass-spectrograph, there has now come the inevitable period of quiescence awaiting the development of new weapons. It thus happens that the period is most remarkable for an unprecedented activity in alchemy, if by such term we designate attempts at transmutation by operations ludicrously inadequate, to all appearance, for such a tremendous task. Fortunately, the epidemic seems on the wane. Although experiments, even the wildest, should never be discouraged, progress is retarded rather than advanced by adopting the least likely, although most sensational, explanation of results. One cannot help feeling that the work expended in the futile attempts to make gold from mercury might have been much more profitably used to develop our knowledge of the structure of atoms along more rational, although more prosaic, lines.

Mass-spectra and Isotopes.

The last of a series of papers [1] on results obtained with the original mass-spectrograph appeared early in the period under review. It contains a complete list of isotopes thus far identified [2] and indicates some of the difficulties in the way of dealing with the remaining elements. Since then fresh discoveries in connexion with isotopic constitution are recorded in the case of two elements only :

Mercury.—The original mass-spectrograph was incapable of resolving the lines of isotopes of this element which differed by one unit, so that the mass-numbers included in the unresolved band

[1] F. W. Aston, *Phil. Mag.*, 1925, [vi], **49**, 1191; *A.*, 1925, ii, 618.

[2] Compare *Ann. Report*, 1924, **21**, 240.

were uncertain. By means of a new and more powerful instrument, these lines have now been clearly resolved and the constitution has been more definitely settled.[3] The mass-numbers and corresponding approximate intensities of the isotopes of mercury are 198(4), 199(5), 200(7), 201(3), 202(10), and 204(2), which are in good accordance with the atomic weight. If other isotopes exist, they must be present in very small proportion.

Sulphur.—In the early work with this element, its principal constituent was shown to be of mass-number 32, and since, with the resolving power then available, this could not be distinguished from 32·06, the atomic weight, it was considered safer to ascribe the fainter satellite lines 33 and 34 to hydrides. Under the increased resolving power of the new instrument, this view is untenable, and it is shown that the latter are really isotopes.[4] This was confirmed by a negative mass-spectrum, obtained by prolonged exposure with both fields reversed, which showed all three lines. S^{34} is about three times more abundant than S^{33}, the two together amounting to about 3% of the whole.

By means of a mass-spectrograph of special design, for which an accuracy of 0·03% is claimed, J. L. Costa [5] has compared the masses of some of the lighter atoms by the method of bracketing. Assuming a standard value of 4·0000 for helium, he obtains for the hydrogen atom a value 1·0079, for the lighter lithium isotope 6·009, and for the carbon atom 12·000. Assuming a value of 14·008 for the nitrogen atom, the heavier isotope of lithium has a mass between 7·010 and 7·013. G. Stetter [6] has combined the principle of the mass-spectrograph with the scintillation method to determine the mass of the high-speed particles—protons—emitted by paraffin when bombarded with α-particles. Using the α-particles themselves as standard, he obtains the expected result corresponding with the theoretical weight of the hydrogen nucleus.

A discovery which may prove of great importance in the future study of mass-rays is that made by C. H. Kunsman [7] that a previously fused mixture of iron oxide and a small quantity of an oxide of an alkali or alkaline-earth metal when used as a hot anode becomes a constant and abundant emitter of singly-charged positive ions of the corresponding metal. Positive ion currents of the order of 10^{-4} amp./cm.^{2} are obtained in a vacuum of 10^{-6} mm.[8] The

[3] F. W. Aston, *Nature*, 1925, **116**, 208; *A.*, 1925, ii, 833.
[4] *Idem*, *ibid.*, 1926, **117**, 893; **A.**, 771.
[5] *Ann. Physique*, 1925, [x], **4**, 425; *A.*, 1925, ii, 1021.
[6] *Z. Physik*, 1925, **34**, 158; *A.*, 1925, ii, 1021.
[7] *Science*, 1925, **62**, 269; **A.**, 218.
[8] H. A. Barton, G. P. Harnwell, and C. H. Kunsman, *Physical Rev.*, [1926, ii], **27**, 739; **A.**, 769.

emission of positive ions from heated salts has also been studied by G. C. Schmidt [9] and H. E. Ives.[10]

By measuring the current carried by the positive ions emitted by lithium, the relative proportions of its two isotopes have been determined.[11] When proper corrections had been applied, Li^7 was found to be 14 times more abundant than Li^6, in good agreement with the accepted atomic weight, 6·94. A method of treatment of photographic plates by partial removal of the gelatin is described[12] by which their sensitivity to the impact of mass-rays is largely increased. Unfortunately, the method is both difficult and uncertain. The keeping properties of the product are also very poor. These plates were, however, essential to the identification of the isotopes of the less favourable elements.

A number of papers dealing with the structure of atoms and isotopes have appeared: H. Stintzing [13] elaborates a system in which all the atomic masses, including those of isotopes, can be represented by a scheme of tetrahedra; R. Reinicke [14] modifies and extends this scheme; H. Nagaoka [15] considers the relation between atomic weight and atomic number, and makes the startling suggestion [16] that within the nucleus of the atom two protons may combine to produce a helium nucleus, the additional two units of mass being produced by the energy absorbed in the process. Other speculative papers on the periodic table are those of D. de Barros,[17] T. Hori,[18] E. W. Washburn,[19] and S. Schtschukarev.[20]

Artificial and Natural Separation of Isotopes.

Few attempts at artificial separation are to be recorded, none of them yielding positive results. J. E. G. Pilley [21] gives a full account of his attempts to separate the isotopes of chlorine and of magnesium by ionic migration in agar gel under a potential of 300 volts, and suggests possible causes of failure. H. Brennen [22]

[9] *Ann. Physik*, 1926, [iv], **80**, 588; **A.**, 877.
[10] *J. Franklin Inst.*, 1926, **201**, 47; **A.**, 218.
[11] M. Morand, *Compt. rend.*, 1926, **182**, 460; **A.**, 331.
[12] F. W. Aston, *Proc. Camb. Phil. Soc.*, 1925, **22**, 548; *A.*, 1925, ii, 706.
[13] *Z. Physik*, 1925, **34**, 686; **A.**, 1926, 7.
[14] *Ibid.*, 1926, **37**, 210; **A.**, 773.
[15] *Proc. Imp. Acad. Tokyo*, 1926, **2**, 112; **A.**, 1075.
[16] *Ibid.*, p. 204; **A.**, 1076.
[17] *Compt. rend.*, 1925, **181**, 719; **A.**, 1926, 7.
[18] *Mem. Coll. Sci. Kyōtō*, 1926, **9**, 371; **A.**, 879.
[19] *J. Amer. Chem. Soc.*, 1926, **48**, 2351; **A.**, 1075.
[20] *Neue Anschauungen in der Chemie*, 1924, **9**, 61; *A.*, 1925, ii, 462.
[21] *Phil. Mag.*, 1925, [vi], **49**, 889; *A.*, 1925, ii, 462.
[22] *Compt. rend.*, 1925, **180**, 282; *A.*, 1925, ii, 174; *Ann. Chim.*, 1925, [x], **4**, 127; *A.*, 1925, ii, 1109.

has investigated the claim [23] that the isotopes of lead could be separated by means of the Grignard reaction, and finds no trace of such effect. T. W. Richards [24] also reports the same result, and, in addition, a failure to separate the isotopes of lead by irreversible evaporation. Ammonium bromide has been subjected to prolonged fractional crystallisation [25] and the atomic weights of the bromine in the final head and tail fractions have been determined. No separation was observed.

In regard to natural separation indicated by inconstancy of atomic weight, chlorine has been further examined by Mlle. E. Gleditsch,[26] W. D. Harkins and S. B. Stone,[27] and A. W. Menzies,[28] but although very wide ranges of terrestrial and meteoric sources were used, no variation was detected. The atomic weight of silicon from various sources has been determined [29] with extreme variations 28·058 and 28·063. Furthermore, the densities of samples of silicon tetrachloride made from similar sources have been measured by a flotation method of extraordinary delicacy.[30] Here the calculated apparent variation of atomic weight for silicon was not greater than 0·005 of a unit.

On the other hand, Briscoe [31] reports a definite variation in the atomic weight of boron from three different sources. Determinations by means of boron trichloride and also density measurements give practically identical results, *viz.*, California, 10·847; Tuscany, 10·823; and Asia Minor, 10·818. A valuable confirmation of this result is afforded by the fact that differences of the same order have been found by O. Hönigschmid (private communication), who gives 10·818, 10·825, 10·840 as the atomic weights yielded by three different samples of boron of unknown origin. This is the first well-substantiated variation of an element, not of radioactive origin, in natural atomic weight. It is interesting to note that if any action leading to separation takes place at all, boron, of all

[23] T. Dillon, R. Clarke, and V. M. Hinchy, *Sci. Proc. Royal Dublin Soc.*, 1922, **17**, 53; *A.*, 1922, ii, 710.

[24] T. W. Richards, H. S. King, and L. P. Hall, *J. Amer. Chem. Soc.*, 1926, **48**, 1530; **A.**, 771.

[25] P. L. Robinson and H. V. A. Briscoe, *J.*, 1925, **127**, 138; *A.*, 1925, ii, 620.

[26] *J. Chim. physique*, 1924, **21**, 456; *A.*, 1925, ii, 174.

[27] *Proc. Nat. Acad. Sci.*, 1925, **11**, 643; *A.*, 1925, ii, 1108; *J. Amer. Chem. Soc.*, 1926, **48**, 938; **A.**, 553.

[28] *Nature*, 1925, **116**, 643; *A.*, 1925, ii, 1109.

[29] H. V. A. Briscoe and P. L. Robinson, *ibid.*, 1926, **117**, 377; **A.**, 331.

[30] P. L. Robinson and H. C. Smith, *J.*, 1926, 1262; **A.**, 771.

[31] H. V. A. Briscoe and P. L. Robinson, *ibid.*, 1925, **127**, 696; *A.*, 1925, ii, 346; H. V. A. Briscoe, P. L. Robinson, and G. E. Stephenson, *ibid.*, 1926, **70**; **A.**, 219.

elements, is the most likely to indicate it, for its two isotopes not only differ by 10% in mass, but are both present in considerable proportion.

Spectra of Isotopes.

Mlle. B. Perrette [32] has compared the line spectrum of ordinary lead of atomic weight 207·2 with that of uranium lead, 206·14, using a vacuum arc in conjunction with a Fabry–Perot interferometer. Differences of the order of 0·007 Å. are found for several lines, in agreement with the earlier work of Merton.[33] F. A. Jenkins [34] has compared the spectra of samples of mercury differing by 0·18 unit in atomic weight and of chlorine differing by 0·097 unit. No real shift of the mercury lines could be observed, but very small shifts, *e.g.*, 0·0012 Å. for 4741 Å., were detected in the case of some of the chlorine lines.

In the region of band spectra, R. S. Mulliken [35] continues his valuable series of papers on the isotope effect. He has studied the band spectra produced by the action of active nitrogen on the halides of copper and shows these are explainable by quantum mechanics. In the case of the iodide, complete data are given and the wavelengths of 260 band heads measured. Every $Cu^{63}I$ band was found, whenever of sufficient resolution and intensity, to be accompanied by a weaker $Cu^{65}I$ band. He has reinvestigated the band spectrum between 3800 and 5300 Å., obtained by Jevons [36] by the action of active nitrogen on silicon tetrachloride, and shows that the emitter must be a molecule SiN. The photographs show that each of the $Si^{28}N$ band heads is accompanied by weaker satellites corresponding to $Si^{29}N$ and $Si^{30}N$ exactly at the theoretically expected positions. W. Jevons [37] has obtained evidence of the isotope effect in the band spectra of the discharge through the vapour of stannic chloride.

Artificial Disintegration and Transmutation.

Continuing their research on the collision of swift α-particles with atomic nuclei, Sir E. Rutherford and J. Chadwick [38] have investigated the scattering of α-particles by a number of elements with the aid of much-improved scintillation methods. Gold, platinum, silver, and copper show no deviation from the simple laws,

[32] *Compt. rend.*, 1925, **180**, 1589; *A.*, 1925, ii, 646.
[33] *Proc. Roy. Soc.*, 1921, [*A*], **100**, 84; *A.*, 1921, ii, 611.
[34] *Nature*, 1926, **117**, 893; **A.**, 771.
[35] *Physical Rev.*, 1925, [ii], **25**, 119; *A.*, 1925, ii, 259; *ibid.*, p. 259; *A.*, 1925, ii, 346; *ibid.*, **26**, 1; *A.*, 1925, ii, 833; *ibid.*, p. 319; *A.*, 1925, ii, 1020; *Nature*, 1925, **116**, 14; *A.*, 1925, ii, 731.
[36] *Proc. Roy. Soc.*, 1913, [*A*], **89**, 187; *A.*, 1913, ii, 813.
[37] *Ibid.*, 1926, [*A*], **110**, 365; **A.**, 222.
[38] *Phil. Mag.*, 1925, [vi], **50**, 889; *A.*, 1925, ii, 1109.

it being assumed that the colliding particles are point charges and that the inverse-square law of force holds. In the case of gold, this was proved true down to distances of approach between $3{\cdot}2 \times 10^{-12}$ and 1×10^{-11} cm. On the other hand, light elements, such as magnesium and aluminium, showed remarkable deviations which were of the same type whether the scattering angle observed was 90° or 135°. No law of force yet proposed seems adequate to explain these results. P. Debye and W. Hardmeier [39] and W. Hardmeier [40] suggest that they are probably due to the incomplete rigidity of the nucleus giving rise to polarisability. The subject is also discussed by A. Smekal [41] and E. Guth.[42]

As has been already reported,[43] Rutherford and Chadwick demonstrated the disintegration of all elements from boron to potassium inclusive, with the exception of carbon and oxygen, and obtained inconclusive results with lithium and beryllium. On the other hand, Kirsch and Pettersson stated that they had succeeded in disintegrating all these four elements, and also claimed that they could distinguish between protons and α-particles by the qualities of the scintillations observed. The Vienna workers have published several papers in support of their claims,[44] and Chadwick [45] has recently reinvestigated several of the points at issue. Using new optical systems of great efficiency, he was unable to detect the emission of protons of a range greater than 4 cm. in air from beryllium, carbon, or oxygen. A very small effect in the case of lithium can be ascribed to traces of impurity. Hence, whatever explanation may be given for the discrepancies between the observations made at Vienna and those made at Cambridge, there seems no doubt that these four elements have nuclei differing in some fundamental way from the others.

In contradistinction to these now well-authenticated cases of transmutation, in which the most violently energetic forces in nature, corresponding to millions of volts, are employed, there are numerous claims of transmutation of one element to another by the use of processes of quite ordinary quality. The most important of these is that of mercury into gold, claimed by Miethe to take place in an ordinary mercury-vapour lamp as already reported.[46] The caution then advised has been amply justified. The claim was

[39] *Physikal. Z.*, 1926, **27**, 196; **A.**, 450.
[40] *Ibid.*, p. 574; **A.**, 990.
[41] *Ibid.*, p. 383; **A.**, 772.
[42] *Ibid.*, p. 507; **A.**, 880.
[43] *Ann. Report*, 1924, **21**, 246.
[44] H. Pettersson and G. Kirsch, *Physikal. Z.*, 1924, **25**, 588; *A.*, 1925, ii, 623; G. Kirsch, *ibid.*, 1925, **26**, 379; *A.*, 1925, ii, 621; *ibid.*, p. 457; *A.*, 1925, ii, 923.
[45] *Phil. Mag.*, 1926, [vii], **2**, 1056; **A.**, 1191.
[46] *Ann. Report*, 1924, **21**, 248.

based upon the idea that it should be quite easy to bring about the collapse of a planetary electron into the positively charged nucleus. As has been pointed out,[47] this is fundamentally unsound. Furthermore, such a process must result in an isobare of atomic number one unit less. Now an examination of all the species of atoms known at present reveals the fact that every pair of isobares known with certainty differs by two units of atomic number, and also that elements of odd and of even atomic number differ fundamentally in their isotopic grouping. There is obviously no evidence for this type of change in nature.

Miethe's claim has been supported by H. Nagaoka,[48] who employed a high-tension condensed discharge between electrodes of mercury and tungsten, immersed in hydrocarbon oils, and detected both silver and gold in the residues. Ultimately, enough of the "transmutation" gold was prepared by Miethe to enable an atomic-weight determination to be made. This was performed by O. Hönigschmid and E. Zintl,[49] and the value obtained was indistinguishable from that of ordinary gold, *viz.*, 197·2. At the same time, mercury was shown by the new mass-spectrograph to contain no appreciable quantity of an isotope of mass-number less than 198 (*vide supra*). In the face of these facts, it became very difficult to defend the transmutation theory, and numerous attempts were made to discover an alternative explanation for the presence of the gold. This led to a lively controversy as to the possibility of freeing mercury from gold by distillation, A. Miethe and H. Stammreich [50] maintaining that this could be done, whilst E. H. Riesenfeld and W. Haase [51] and W. Venator [52] took the opposite view. Miethe's experiments [53] were repeated by A. Piutti and E. Boggio-Lera,[54] who obtained negative results, and by F. Haber, J. Jaenicke, and F. Matthias,[55] who were satisfied that the minute traces of gold they found could be attributed to the materials employed. The same result was obtained by E. Tiede, A. Schleede, and F. Goldschmidt.[56]

The experiments of M. W. Garrett [57] are particularly convincing.

[47] *Ann. Report, loc. cit.*

[48] *Nature*, 1925, **116**, 95; *A.*, 1925, ii, 835; *J. Phys. Radium*, 1925, [vi], **6**, 209; *A.*, 1925, ii, 1111.

[49] *Z. anorg. Chem.*, 1925, **147**, 262; *A.*, 1925, ii, 924.

[50] *Ibid.*, 1925, **149**, 263; **A.**, 119; *Ber.*, 1926, **59**, [*B*], 359; **A.**, 493.

[51] *Ibid.*, 1925, **58**, [*B*], 2828; **A.**, 264; *ibid.*, 1926, **59**, [*B*], 1625; **A.**, 922.

[52] *Z. angew. Chem.*, 1926, **39**, 229; **A.**, 486.

[53] A. Miethe and H. Stammreich, *Z. anorg. Chem.*, 1926, **150**, 350; **A.**, 367.

[54] *Giorn. Chim. Ind. Appl.*, 1926, **8**, 59; **A.**, 699.

[55] *Z. anorg. Chem.*, 1926, **153**, 153; **A.**, 699.

[56] *Ber.*, 1926, **59**, [*B*], 1629; **A.**, 922.

[57] *Nature*, 1926, **118**, 84; **A.**, 773; *Proc. Roy. Soc.*, 1926, [*A*], **112**, 391; **A.**, 1015.

Using every precaution, he repeated Miethe's experiments, but even after an interrupted arc had been run for 288 hours in a silicon tube containing mercury and hydrogen, no gold could be found. The test employed was so delicate that he could have detected one ten-thousandth part of the quantity of gold which Miethe's results led one to expect. Garrett also attempted to prepare indium from tin, and scandium from titanium, in each case with negative results. Other contributions to the subject are made by L. Kaul,[58] F. Stumpf,[59] A. S. Russell,[60] (Miss) A. C. Davies and F. Horton,[61] and E. Duhme and A. Lotz.[62] The balance of the experimental results is unmistakably in support of the theoretical conclusion that the introduction of an electron into a nucleus is not to be brought about by such means.

Other claims of transmutation are of a more extravagant nature and may safely be set aside awaiting confirmation. R. W. Riding and E. C. C. Baly [63] state that they are able to disintegrate nitrogen by cathode-ray bombardment and that the result of this is the formation of helium and neon. A. Smits [64] claims to have transmuted lead into mercury and thallium in an arc, and F. Paneth and K. Peters [65] have come to the surprising conclusion that hydrogen may be turned into helium by dissolving it in palladium. Unless all modern views of the stability of atomic nuclei are wrong, it would appear that in all these cases the presence of an element has been mistaken for its creation.

Radiation and the Structure of the Nucleus.

The magnetic spectra of primary β-rays emitted by radioactive nuclei, and of secondary β-rays produced by γ-rays, have been widely studied. The most important result is a definite proof that in the β-ray type of disintegration the emission of the γ-ray takes place after the ejection of the electron from the nucleus. Fifteen lines of low energy from 4290—12,670 volts in the β-ray spectrum of radium-*B* were measured by D. H. Black.[66] On analysis of the values so obtained, it was found that eleven of these corresponded to an atom of number 83, whilst with an atom of number 82 it was possible to account for only six of them. This suggested that the original measurements of Rutherford and Andrade

[58] *Chem. Zentr.*, 1924, ii, 1049; *A.*, 1925, ii, 177.
[59] *Z. Physik*, 1924, **30**, 173; *A.*, 1925, ii, 619.
[60] *Nature*, 1925, **116**, 312; *A.*, 1925, ii, 924.
[61] *Ibid.*, 1926, **117**, 152; **A.**, 221.
[62] *Ber.*, 1926, **59**, [*B*], 1649; **A.**, 930.
[63] *Proc. Roy. Soc.*, 1925, [*A*], **109**, 186; *A.*, 1925, ii, 925.
[64] *Nature*, 1926, **117**, 13; **A.**, 106.
[65] *Ber.*, 1926, **59**, [*B*], 2039; **A.**, 1077.
[66] *Proc. Camb. Phil. Soc.*, 1925, **22**, 832, 838; **A.**, 1926, 6.

in 1914 of the natural γ-ray spectrum of radium-*B*, which corresponded with an atom of number 82, were probably erroneous. These observations were therefore repeated,[67] the original rock-salt crystal method being used. The new results were in exact accord with Coster's data for an element of number 83. Furthermore, the energies of the three main γ-rays from radium-*B* and the strongest from radium-*C* were measured by C. D. Ellis and W. A. Wooster [68] to an accuracy of 1%. These results were also in agreement with those calculated on the view that the emission follows the nuclear disintegration. O. Hahn and Frl. L. Meitner [69] have measured the β-ray spectrum of radioactinium and its products, and from their results the energies and wave-lengths of the γ-rays from radioactinium, actinium-*X*, and actinium-*C''* are calculated by Meitner,[70] and shown to be those expected from the atom resulting from the α- and β-ray changes and not from the original atom, thus confirming the results of the Cambridge workers. C. D. Ellis and W. A. Wooster [71] give a further discussion of the β-ray type of disintegration in which the view of Meitner, that γ-rays are emitted during the reorganisation of the nucleus after the disturbance caused by the disintegration electron, is extended to the idea that the γ-rays are emitted by the electronic system of the nucleus. Discussions on the origin of continuous and other β-ray spectra are given by A. Piccard [72] and by J. Thibaud.[73] The latter concludes that Einstein's numerical relation between the energy of a γ-ray and that of the electron which it excites is completely verified. He is unable to find any evidence of the *J*-electron level of Barkla.

Radium Products.—The natural β-ray spectrum of radium-*B* and -*C* has been mapped out by J. d'Espine,[74] who observed a band of high-velocity particles with $H\rho$ values between 15,000 and 27,000, and gives a table of lines which agree with those already given by Ellis and Skinner.[75] A direct determination of the distribution of intensity in this spectrum was started by L. F. Curtiss.[76] This work has been continued with improved apparatus by R. W.

[67] (Sir) E. Rutherford and W. A. Wooster, *Proc. Camb. Phil. Soc.*, 1925, **22**, 834; **A.**, 1926, 6.

[68] *Ibid.*, p. 844; **A.**, 1926, 6. [69] *Z. Physik*, 1925, **34**, 795; **A.**, 105.

[70] *Ibid.*, p. 807; **A.**, 1926, 106.

[71] *Proc. Camb. Phil. Soc.*, 1925, **22**, 849; **A.**, 1926, 6.

[72] *J. Phys. Radium*, 1925, [vi], **6**, 334; **A.**, 1926, 106.

[73] *Compt. rend.*, 1924, **179**, 815; *A.*, 1925, ii, 257; *ibid.*, 1925, **180**, 138; *A.*, 1925, ii, 176; *J. Phys. Radium*, 1925, [vi], **6**, 334; **A.**, 1926, 106; *Ann. Physique*, 1926, [x], **5**, 73; **A.**, 333.

[74] *Compt. rend.*, 1925, **180**, 1403; *A.*, 1925, ii, 622.

[75] *Proc. Roy. Soc.*, 1924, [*A*], **105**, 60; *A.*, 1924, ii, 85; *ibid.*, p. 165; *A.*, 1924, ii, 137.

[76] *Proc. Camb. Phil. Soc.*, 1925, **22**, 597; *A.*, 1925, ii, 622.

Gurney,[77] whose measurements lead to the conclusion that both radium-*B* and radium-*C* possess a genuine continuous β-ray spectrum quite distinct from the line spectrum which is superposed upon it. The latter is attributed to the conversion of γ-rays into β-rays, the probability of which is about 1 to 7. The natural β-ray spectrum of radium-*D* has been mapped out by L. F. Curtiss,[78] and that of radium-*E* by (Mlle.) I. Curie and J. d'Espine.[79]

Thorium Products.—The β-ray spectrum of thorium disintegration products has been examined by W. Pohlmeyer [80] and by D. H. Black.[81] The latter gives measurements of 17 lines ascribed to thorium-*B*, that at Hρ 1398 being extremely strong. For thorium-*C* and -*D*, 16 lines were measured, the strongest being Hρ 541. A group of lines of very high energies of more than $2{\cdot}5 \times 10^6$ volts was recorded, probably due to thorium-*D* and arising from the conversion of a single γ-ray in the *K* and *L* levels of the atom. Quantitative measurements of this spectrum have been carried out by R. W. Gurney [82] in continuation of his work with the radium products (*vide supra*). The results suggest a law of "β-ray disintegration," namely, that no γ-rays of high energy can be emitted by those radioactive substances which expel their nuclear electrons with low energies. The probability that a γ-ray of 150,000 volts energy emitted by thorium-*B* is converted in the *K* level is at least 1 in 4. For the γ-ray of 40,000 volts from thorium-*D*, the probability of conversion in the *L* level is more than 1 in 5.

A rapid method of purifying mesothorium-2 from its mixtures is described by D. K. Yovanovitch,[83] and its magnetic spectrum is found to contain 43 lines of energies between 8×10^6 and $3{\cdot}9 \times 10^4$ volts. The primary β-ray spectrum of mesothorium-2 has also been studied by J. Thibaud [84] and found to be similar to the secondary β-ray spectrum of element 89, according to theory. A further study of the secondary β-ray spectrum from lead gave two lines in the γ-radiation of 333 and 459 k.v. respectively, confirming the results of M. de Broglie and Cabrera.[85] The relation between the

[77] *Proc. Roy. Soc.*, 1925, [*A*], **109**, 540; **A.**, 1926, 5.
[78] *Physical Rev.*, 1926, [ii], **27**, 257; **A.**, 450.
[79] *Compt. rend.*, 1925, **181**, 31; *A.*, 1925, ii, 732.
[80] *Z. Physik*, 1924, **28**, 216; *A.*, 1925, ii, 347.
[81] *Nature*, 1925, **115**, 226; *A.*, 1925, ii, 177; *Proc. Roy. Soc.*, 1925, [*A*], **109**, 166; *A.*, 1925, ii, 922.
[82] *Ibid.*, 1926, [*A*], **112**, 380; **A.**, 990.
[83] *J. Chim. phys.*, 1926, **23**, 1; **A.**, 331 [compare (Mlles.) E. Gleditsch and C. Chamie, *Compt. rend.*, 1926, **182**, 380; **A.**, 332].
[84] *Compt. rend.*, 1924, **179**, 1322; *A.*, 1925, ii, 85.
[85] *Ibid.*, 1923, **176**, 295; *A.*, 1923, ii, 109.

intensity of excited β-ray emission and atomic number has been worked out by M. de Broglie and J. Thibaud.[86]

Heat developed in Radioactivity.

The increase in the heating effect of radium preparations over a period of $16\frac{3}{4}$ years has been measured by Mme. M. Curie and D. K. Yovanovitch [87] and shown to amount to 11%. This is proved to be that theoretically expected from the growth of polonium.

The distribution of energy developed by different types of radiation has been investigated by J. Thibaud.[88] Taking Rutherford and Robinson's value [89] for the total heat set free from 1 g. of radium in radioactive equilibrium, *viz.*, 135—137 cal./hr., and calculating the kinetic energy of α-particles and recoil effects as 117·7 cal. and of β-radiation as 12·1 cal., he ascribes the balance of about 7 cal. to γ-radiations. He points out that the latter will not be of constant frequency, but that their relative intensities enable a mean quantum to be calculated. In this way, the mean quanta of γ-radiation from radium-*B*, radium-*C*, and radium are given as 302, 1010, and 187 k.v., respectively. The value for *Z*, the number of atoms disintegrating per second, being taken as $3{\cdot}57 \times 10^{10}$, the total energy of the γ-rays is 7·27 cal./hr. The agreement of this figure with the balance above is taken to support the hypothesis that each α-particle emission from the nucleus is followed by a single γ-ray.

An elegant balance method, by which the small heating effect of γ-rays may be directly measured in the presence of the α-rays, has been worked out by C. D. Ellis and W. A. Wooster.[90] This consists in measuring the difference in rise of temperature of aluminium and lead blocks exposed to the mixed rays. The α-rays, being completely absorbed, produce the same heating effect in each metal, but a differential effect is produced by the γ-rays owing to the higher absorbing power of the lead. By this means they have measured the total γ-ray energy from one curie of radium-*B* and radium-*C* to be $8{\cdot}6 \pm 0{\cdot}4$ cal./hr. From the absorption coefficients of Ahmad,[91] the γ-ray energies are in the ratio of 1 to 9, so that, of the above figure, 0·86 cal./hr. is attributed to radium-*B* and 7·7 cal./hr. to radium-*C*, corresponding with 185 and 1660 k.v., respectively.

[86] *Compt. rend.*, 1925, **180**, 179; *A.*, 1925, ii, 165 (compare Ellis, *Proc. Roy. Soc.*, 1921, [*A*], **99**, 261; *A.*, 1921, ii, 422).

[87] *J. Phys. Radium*, 1925, [vi], **6**, 33; *A.*, 1925, ii, 464.

[88] *Compt. rend.*, 1925, **180**, 1166; *A.*, 1925, ii, 464.

[89] *Phil. Mag.*, 1913, [vi], **25**, 312; *A.*, 1913, ii, 269.

[90] *Proc. Camb. Phil. Soc.*, 1925, **22**, 595; *A.*, 1925, ii, 622.

[91] *Proc. Roy. Soc.*, 1924, [*A*], **105**, 507; *A.*, 1924, ii, 440; *ibid.*, **106**, 8; *A.*, 1924, ii, 582.

R. W. Lawson [92] points out that the value obtained by Hess of 25·2 cal./hr. for the total heat developed by 1 g. of radium free from its disintegration products, when corrected for the γ-ray energy lost, becomes 25·5 cal./hr., a figure much better in accordance with the value $3{\cdot}72 \times 10^{10}$ for Z than with the lower value $3{\cdot}40 \times 10^{10}$.[93]

A. Holmes and R. W. Lawson [94] have made a complete and very interesting investigation into the effect of the radioactivity of potassium and rubidium in geological heat-development. For this purpose, they take for the velocity of the β-rays $0{\cdot}90c$ and $0{\cdot}60c$, and the half-periods $1{\cdot}5 \times 10^{12}$ and $1{\cdot}0 \times 10^{11}$ years, respectively. The extreme rarity of rubidium renders its effect negligible, but owing to the high abundance of potassium relative to uranium and thorium, its effect is in the aggregate of the same order of importance as that of these vastly more active elements.

α-Rays.

A very complete investigation of the ionisation caused by α-particles in different gases has been made by R. W. Gurney,[95] who has measured the total ionisation produced by beams of α-particles of definite energy in xenon, krypton, argon, neon, helium, oxygen, hydrogen, and nitrogen. Particles of residual ranges from 7—18 cm. were employed, the former limit being imposed by the small quantities of krypton and xenon available. In the five monatomic gases, the ionisation increases with increasing atomic number, a result to be expected from the decreasing ionisation potential. It is less in the diatomic gases, indicating that the energy is expended in other ways. The ratios found for different gases are not independent of the velocities of the α-particles. Gurney [96] has also measured the stopping powers of the five rare gases and of hydrogen and oxygen, which are in good agreement with those calculated by R. H. Fowler.[97]

(Mlle.) I. Curie [98] has published a series of papers on the variation of range, initial velocity, and ionising power of the α-particles from polonium; the experiments were done in oxygen and nitrogen, and it is concluded that three-quarters of the α-particles have velocities differing by less than 0·3%. The initial velocity is given

[92] *Nature*, 1925, **116**, 897; **A.**, 1926, 5.

[93] *Ann. Report*, 1924, **21**, 253; H. Geiger and A. Werner, *Z. Physik*, 1924, **21**, 187; *A.*, 1924, ii, 226.

[94] *Nature*, 1926, **117**, 620; **A.**, 554; *Phil. Mag.*, 1926, [vii], **2**, 1218.

[95] *Proc. Roy. Soc.*, 1925, [*A*], **107**, 332; *A.*, 1925, ii, 256.

[96] *Ibid.*, p. 340; *A.*, 1925, ii, 256.

[97] *Proc. Camb. Phil. Soc.*, 1925, **22**, 793; *A.*, 1925, ii, 834 (compare L. Loeb and E. Condon, *J. Franklin Inst.*, 1925, **200**, 595; **A.**, 1926, 5).

[98] *Compt. rend.*, 1924, **179**, 761; *A.*, 1925, ii, 175; *ibid.*, 1925, **180**, 831; *A.*, 1925, ii, 348; *Ann. Physique*, 1925, [x], **3**, 299; *A.*, 1925, ii, 834.

as $1{\cdot}593 \times 10^9$ cm./sec. In air, the range is 3·87 cm., and maximum ionisation occurs at 4·5 mm. from the end. The velocity at that point is $0{\cdot}57 \times 10^9$ cm./sec.

The stopping powers of various metals for α-particles have been measured by J. Consigny.[99] For speeds of $1{\cdot}59$ to $1{\cdot}09 \times 10^9$ cm./sec., the logarithms of the stopping powers, when plotted against atomic numbers and atomic weights, give straight lines of slopes $\tan^{-1} 0{\cdot}552$ and 0·5, respectively. S. Rosenblum,[1] however, from similar work, concludes that, except for platinum, the mass per unit area which reduces the speed of the α-particle by the same fraction is a linear function of the atomic number. The single scattering of α-particles by gold foil has been measured for small angles by D. C. Rose.[2] His curves indicate that the *K*-shell is not ionised to any appreciable extent.

Continuing his work [3] on the capture and loss of electrons by α-particles, G. H. Henderson [4] has determined quantitatively the ratio of the number of doubly-charged to the number of singly-charged particles in equilibrium. He finds that this is independent of the material through which the α-particles have passed. J. C. Jacobsen [5] gives measurements of the mean free path for capture and loss of electrons by α-particles in air and hydrogen. From these, he concludes that the probability of capture of electrons is considerably greater in air than in hydrogen under conditions in which that of loss is the same.

In a series of papers, S. C. Lind and D. C. Bardwell [6] describe chemical action brought about by the influence of α-particles from radon (niton). The velocity coefficients of the reaction these bring about in electrolytic gas show interesting variations with pressure. Saturated hydrocarbons condense, methane and carbon dioxide combining to form a wax-like solid. Similar actions by the β- and γ-rays of radium have been studied by J. Errera and V. Henri.[7]

Long-range Particles.—The ratio of the number of long-range particles to the number of α-particles of ordinary range from polonium deposited on various metals has been measured by (Mlle.) I. Curie and N. Yamada.[8] They state that the number of long-range

[99] *Compt. rend.*, 1926, **182**, 1614; **A.**, 772; *ibid.*, **183**, 127; **A.**, 879.

[1] *Ibid.*, p. 198; **A.**, 879. [2] *Proc. Roy. Soc.*, 1926, [*A*], **111**, 677; **A.**, 880.

[3] *Ibid.*, 1923, [*A*], **102**, 496.

[4] *Ibid.*, 1925, [*A*], **109**, 157; *A.*, 1925, ii, 922.

[5] *Nature*, 1926, **117**, 858; **A.**, 655.

[6] *J. Amer. Chem. Soc.*, 1924, **46**, 2003; *A.*, 1924, ii, 840; *ibid.*, 1925, **47**, 2675; **A.**, 1926, 4; *ibid.*, 1926, **48**, 2335; **A.**, 1077.

[7] *J. Phys. Radium*, 1926, [vi], **7**, 225; **A.**, 1077.

[8] *Compt. rend.*, 1925, **180**, 436; *A.*, 1925, ii, 255; *ibid.*, p. 1487; *A.*, 1925, ii, 621; *J. Phys. Radium*, 1925, [vi], **6**, 376; **A.**, 1926, 220.

particles is roughly proportional to the quantity of polonium. In oxygen and carbon dioxide, their number is roughly 10 per 10^7 α-particles. In air, there are about three times as many.[9] The α-rays from thorium-*C* and thorium-*C'* have been studied by (Frl.) L. Meitner and K. Freitag,[10] using a special form of Wilson apparatus. The ratio of the number of α-particles from thorium-*C* to those from thorium-*C'* was 34·3 : 65·7, and the observed ranges in different gases were in agreement with the values calculated by Bohr. Long-range particles of ranges 9·5 and 11·5 cm. were in the proportion of about 70 and 200, respectively, per million of the whole. The tracks of range longer than 20 cm. were much finer and are ascribed to protons. Similar work has been carried out by K. Philipp,[11] who confirms these results.[12]

Radioactive Constants.

L. Bastings [13] has determined the decay constant of radium-*E*, $\lambda = 0{\cdot}139$ day^{-1}, corresponding with a half-period of 4·98 days. This value is challenged by G. Fournier,[14] who employs a piezo-electrometer and obtains for three different sources values of 4·86, 4·86, and 4·84 days, supporting the original value 4·85 given by Thaller. On the other hand, L. F. Curtiss [15] estimates the half-period as 5·07 days, in agreement with the results of Antonof, Meitner, and Bastings. The decay constant of radon has also been measured by Bastings,[16] who for its half-period gives 3·833 days, a slightly higher value than that previously given by Curie and Chamié.[17] B. Batscha [18] estimates the half-period of thoron at about 53 seconds. W. P. Widdowson and A. S. Russell [19] have investigated mesothorium-2 and ascribe to it a half-period of 5·95 hours, 4% lower than that obtained by Hahn.[20] P. Bracelin's [21] measurements of the half-period of radium-*B* and radium-*C* give for the former from 26·7 to 26·8 min., and for the latter 19·72 ± 0·04 min. A. W. Barton,[22] using a modification of Jacobsen's

[9] Compare Bates and Rogers, *Nature*, 1923, **112**, 435; *A.*, 1923, ii, 720; *Proc. Roy. Soc.*, 1924, [*A*], **105**, 97, 360; *A.*, 1924, ii, 84, 296.
[10] *Z. Physik*, 1926, **37**, 481; **A.**, 772.
[11] *Ibid.*, p. 518; **A.**, 772.
[12] Compare S. Rosenblum, *Compt. rend.*, 1925, **180**, 1332; *A.*, 1925, ii, 463.
[13] *Phil. Mag.*, 1924, [vi], **48**, 1075; *A.*, 1925, ii, 9.
[14] *Compt. rend.*, 1925, **181**, 502; *A.*, 1925, ii, 1110.
[15] *Physical Rev.*, 1926, [ii], **27**, 672; **A.**, 771.
[16] *Proc. Camb. Phil. Soc.*, 1925, **22**, 562; *A.*, 1925, ii, 621.
[17] *J. Phys. Radium*, 1924, [vi], **5**, 238; *A.*, 1925, ii, 8.
[18] *Z. physikal. chem. Unterr.*, 1924, **37**, 117; *A.*, 1925, ii, 177.
[19] *Phil. Mag.*, 1925, [vi], **49**, 137; *A.*, 1925, ii, 463.
[20] *Physikal. Z.*, 1908, **9**, 245; *A.*, 1908, ii, 454.
[21] *Proc. Camb. Phil. Soc.*, 1926, **23**, 150; **A.**, 553.
[22] *Phil. Mag.*, 1926, [vii], **2**, 1273.

apparatus for the investigation of the decay constant of radium-*C'*, confirms the existence of this body and estimates its half-period to be of the order of 10^{-6} second. The average life-period of ionium has been found to be 29,000 years by O. Koblic,[23] who assumes Hönigschmid's figure for the ionium–thorium ratio.

W. D. Harkins and W. G. Guy [24] have measured the radioactivity of many elements by a very delicate balance method. Twenty-five of these gave an activity less than $3{\cdot}3 \times 10^{-6}$ that of uranium. They conclude that rubidium is 1·39 times as radioactive as potassium, but the radiation from rubidium is 10 to 15 times less penetrating than that from potassium, hence their activities cannot be traced to a common source. (Mlle.) S. Maracineanu [25] makes the remarkable announcement that the activity of uranium oxide is altered by as much as 50% by exposure to sunlight, and that ordinary lead acquires radioactive properties by the same treatment. This will need very strong confirmation, for it is contrary to all accepted views.

Cosmic Rays and Stellar Matter.

The original discovery by Kolhörster that exceedingly penetrating rays were detectable at high altitudes has led to very interesting results. Although G. Hoffmann [26] and F. Běhounek [27] consider that at sea level all the radiation observed can be explained as coming from known radioactive sources, and that the experiments of L. Myssovski and L. Tuwim [28] are not conclusive, yet R. A. Millikan [29] has obtained proofs of the presence of penetrating extra-terrestrial radiation at high altitudes of a reasonably unambiguous character. In his latest communication on the subject,[30] he describes the results obtained by sinking two specially designed electroscopes in high-altitude snow lakes. The readings obtained in two lakes at different altitudes are perfectly consistent with each other, when allowance is made for the absorption by the air between, and can only be explained by the presence of two types of radiation of unprecedented hardness directed towards the earth from outer space. The coefficients of absorption give wave-lengths 0·00038 Å. and 0·00063 Å. The former corresponds to 32×10^6 volts, about 50 times the

[23] *Chem. Listy*, 1925, **19**, 389; **A.**, 105.

[24] *Proc. Nat. Acad. Sci.*, 1925, **11**, 628; *A.*, 1925, ii, 1109.

[25] *Bull. Acad. Sci. Roumaine*, 1924, **9**, [3—4], 1; *A.*, 1925, ii, 348; *Compt. rend.*, 1925, **181**, 774; **A.**, 6.

[26] *Physikal. Z.*, 1925, **26**, 669; *A.*, 1925, ii, 1110; *ibid.*, 1926, **27**, 291; **A.**, 656.

[27] *Ibid.*, p. 8 (compare V. F. Hess, *ibid.*, p. 159; **A.**, 450).

[28] *Z. Physik*, 1925, **35**, 299; **A.**, 221.

[29] *Science*, 1925, **62**, 446; **A.**, 450.

[30] R. A. Millikan and G. Harvey Cameron, *Physical Rev.*, 1926, **28**, 851.

frequency of γ-rays. These should be capable of producing secondary β-rays which could penetrate brass walls 5 mm. thick. They are, nevertheless, only about one-thirtieth of the frequency of radiation expected to result from the simultaneous annihilation of one proton and one electron.[31]

In connexion with these cosmic rays it is of interest to note that astronomers have long decided that the only possible way in which the stars can maintain their radiation is by some process of annihilation of the matter of which they are composed. In attempting to postulate physical conditions under which ordinary matter might be expected to behave in this way, very formidable difficulties are encountered. J. H. Jeans [32] does away with these entirely by boldly postulating that matter as we know it cannot, under any conceivable conditions, transmute itself into radiation, and that the interior of stars, that is, the vast bulk of the material universe, contains elements of a type unknown and unknowable on earth. He supposes that these have atomic weights as high as 300, and that in their atoms a planetary electron is capable of collapsing into the nucleus and simultaneously annihilating itself and a proton in that process. In order to avoid explosive instability, he makes the ingenious hypothesis that, as soon as the temperature rises so high that all the planetary electrons are stripped from the nucleus, the operation becomes impossible. This theory covers most of the facts, but the quality of cosmic radiation, which is the only form of information on the point that we can get from the stars at present, seems to indicate a more gradual type of degradation.

F. W. Aston.

[31] M. Home, *Nature*, 1926, **117**, 194; **A.**, 221.
[32] *Nature*, 1926, **118**, [Supp.], 29.

SPECTROSCOPY.

There have been several well-marked stages in the development of spectroscopy, and during some of these the chemical importance of the subject has certainly been small. This is not true of its present aspect, and it seems probable that its chemical interest will continue to increase for some time. In the years following the pioneer investigations of Bunsen and Kirchoff, the interest lay in such work as the assignment of the many new spectra to the elements and compounds responsible for them. This led to important chemical discoveries, and, in particular, to the recognition of new elements. The second phase of the subject was marked by important instrumental improvements—the introduction of high-dispersion spectroscopes, interferometers, etc.—rather than by new theories or discoveries. With the aid of these improved instruments, trustworthy wave-length standards were constructed, and by 1913, when this phase ended, about 100,000 lines had been measured with tolerable accuracy. In spite of this industry, scarcely any progress had been made with a theory of spectra, and the catalogues of lines in Kayser's " Handbuch der Spectroscopie " are a sufficient demonstration of the state of the subject in the absence of any co-ordinating theory. Within the last twelve years, the quantum theory of spectra has proved itself competent to establish order, and even spectra as complex as that of the iron arc have been disentangled into related groups of lines on an ordered plan. The uses of the new theory are not limited to formal spectroscopy. A theory of atomic structure has been based upon it; and problems of valency and molecular structure, which have intrigued many generations of chemists, may be solved by its further application.

The growth of spectroscopy in all its branches has recently been so rapid that a brief report of this nature must, in any case, be inadequate. The material selected for review has been chosen to cover the very varied chemical interests of the subject.

The Interpretation of Line Spectra.

From the chemist's standpoint, the most important product of the study of line spectra is a useful atomic model. It is, of course, doubtful whether anything so crude as a model can adequately represent those changes of atomic configuration which apparently

produce spectra, but the approximations to reality which can certainly be achieved are in any case invaluable.

The empirical facts of line spectra are briefly these. The complete line spectrum of an element consists of a number of series, and the component lines of each series are connected by a simple expression. In the hydrogen spectrum, which is the simplest of all, the expression takes the form

$$\nu = N(1/n^2 - 1/m^2),$$

where n and m have integral values, and N is the "Rydberg constant." Replacing n by the values 1, 2, 3, and 4, and m by suitable sequences of integers, four series are obtained corresponding to known lines in the far ultra-violet ($n = 1$), the visible and near ultra-violet ($n = 2$), and the infra-red ($n = 3$ and 4 *). The same simple expression, with N replaced by $4N$, gives the frequencies of the series lines of ionised helium. The empirical expression, even in an approximate form, for the series emitted by more complex atoms contains two more constants, and becomes

$$\nu = N[1/(n + \mu_1)^2 - 1/(m + \mu_2)^2],$$

where μ_1 and μ_2 are fractional constants. The spectrum of each element contains various series, in each of which μ_1 and μ_2 have characteristic values (principal, diffuse, sharp, etc., series), and, further, each series may be composed of doublets, triplets, or of still more complex groups of lines.†

No theory of these regularities could be developed on the basis of classical mechanics; in fact, it was difficult to account in this way even for the existence of sharp lines in a spectrum, quite apart from their distribution. The general belief, which has proved erroneous, was that an atom must possess characteristic vibration periods corresponding to the frequencies of its spectral lines. This standpoint was abandoned in the successful Bohr theory, first published in 1913. The two terms which appear in the empirical expression for a series line (*e.g.*, N/n^2 and N/m^2 for the hydrogen lines) are now correlated with two states of the atom, with different internal energies. The line is supposed to be emitted owing to a change from the state with the greater energy W_1 to that with the less W_2 (by a mechanism still obscure) and the liberated energy appears as a quantum of light of a definite frequency given by $h\nu = W_1 - W_2$. The internal-energy changes in the atom

* This fourth series was predicted by Bohr, and observed by F. S. Brackett (*Astrophys. J.*, 1922, **56**, 154; *A.*, 1923, ii, 103).

† For full discussion of these regularities, see A. Fowler, "Report on Series Spectra," 1922, Physical Society of London; and F. Paschen and R. Götze, "Seriengesetze der Linienspectren," 1922, Springer, Berlin.

are taken to be due to variations in the orbits of the valency electrons. It was found that the series relationship could be accounted for with the further assumption that only orbits with certain radii are possible "stationary states," *viz.*, those for which the angular momentum of the system is a multiple of a fixed unit. A definite quantum number, corresponding to this multiple, was ascribed to each orbit. This quantum number determines roughly the size of the orbit, and is now called the "principal quantum number." Bohr was at once enabled to calculate the value, N, of the Rydberg constant, to account for the line spectrum of hydrogen, and to predict the spectra of singly-ionised helium and doubly-ionised lithium.

The theory could, in fact, account for the spectral behaviour of the simple systems consisting of a nucleus with a charge e, $2e$, $3e$, etc., accompanied by a solitary planetary electron. In considering such atoms, the motions of the electron could be treated as if controlled by a pure Coulomb (or inverse-square) attraction from a point nucleus, and the orbits were therefore taken to be ellipses, with the circle as a special case. It was soon realised that this simple treatment could not be continued in the extension of the theory to more complex atoms, or even in the explanation of the fine structure of the hydrogen lines, revealed under high dispersion. The presence of other electrons in addition to the radiating one disturbs the simple Coulomb field, and the effect of this perturbation, it has been shown, is to cause a uniform precession of the major axis of the elliptical orbits in their own plane.* This precessional frequency must vary with the ratio of the major to the minor axis, becoming greater as this ratio increases. It has been found that by introducing a second quantum number controlling the ratio of the axes, and therefore also the precessional frequency, some of the regularities in the spectra of complex atoms can be accounted for. This second quantum number is called the "azimuthal quantum number." In effect, each of the original Bohr orbits, with a given principal quantum number, is thus replaced by a group of orbits of different ellipticities, and with azimuthal quantum numbers 1, 2, 3, 4, etc. The energy of each orbit in a group will be different, the amount depending on the degree of perturbation of the central field. These differences are correlated with the appearance of the constants μ_1 and μ_2 in the series formula given above. In each sequence of terms of the type $N/(m + \mu)^2$,

* The disturbing force in the hydrogen atom is taken to be the relativistic change of mass of the electron, due to its varying velocity in an elliptical orbit. This perturbation is, of course, of a much smaller order than that produced by the presence of other electrons. The latest views on the hydrogen spectrum are discussed by A. Sommerfeld in "Three Lectures on Atomic Physics," 1926, Methuen.

the azimuthal quantum number (*i.e.*, the " ellipticity " of the orbits) is regarded as remaining constant, whilst the principal quantum number (*i.e.*, the size of the orbits) takes all possible values. The separate existence of the principal, diffuse, etc., series of an element is therefore due to the precessional motion of the electron in a non-Coulomb field, and all such series should coincide in the spectrum of an atom in which there is no perturbation of the field—a condition nearly realised in the hydrogen atom.

The occurrence of doublets, triplets, etc., in series spectra still lacked a theoretical interpretation. This was provided in 1920 by Sommerfeld with the introduction of a third or " inner " quantum number. Shortly afterwards, M. A. Catalán [1] discovered that the spectra of some elements, such as manganese and chromium, contain groups of lines of previously unsuspected complexity such as septets and octets. These " multiplets " were found to fit the scheme of " inner quantum numbers " devised for the simpler groups. This third quantum number was introduced in a purely formal manner, but the necessity for its introduction is regarded as an indication of a precession of the orbital plane of the electron about the invariant axis of the atom. To deal with the Zeeman effect and other phenomena, at least one more quantum number must be added to the previous three, so that at present an electronic orbit is considered to require four suitably chosen quantum numbers for its complete description. There is a difficulty in finding a physical interpretation for the fourth quantum number, as an electron has always been treated as a point-mass with only three degrees of freedom. The explanation has been offered [2] that the dimensions of the electron must also be taken into account, and that it may possess energy in virtue of a spinning motion about an axis of rotation in the electron itself. There is little doubt, however, that additional quantum numbers will be found necessary for the complete description of spectroscopic observations,[3] and it is clear that the importance of the physical model is at present diminishing and that many developments in spectroscopic theory are now proceeding along purely formal lines. The resources of the model, nevertheless, are by no means exhausted, as the investigation of H. N. Russell and F. A. Saunders [4] into the arc spectra of the alkaline earths has

[1] *Phil. Trans.*, 1922, [*A*], **223**, 127; *A.*, 1922, ii, 726.

[2] Compare G. E. Uhlenbeck and S. Goudsmit, *Nature*, 1926, **117**, 264; **A.**, 215.

[3] Compare A. E. Ruark and R. L. Chenault, *Phil. Mag.*, 1925, [vi], **50**, 937; *A.*, 1925, ii, 1103, and the introduction of a " fine quantum number " to account for line satellites.

[4] *Astrophys. J.*, 1925, **61**, 38; *A.*, 1925, ii, 911. See also A. E. Ruark, *J. Opt. Soc. Amer.*, 1925, **11**, 199; *A.*, 1925, ii, 1016.

recently proved. These spectra contain series which do not fit into the ordinary series scheme, and yet are related to it, as shown by the triplet separations, etc., and the terms expressing these additional series have been called "anomalous terms," or "primed terms." It has been found that these spectra can be accounted for in terms of the model by postulating simultaneous changes in the orbits of *both* the valency electrons of the alkaline earths; the frequency of the line emitted is determined by the algebraic sum of the energy changes involved. This pretty extension of the original theory [5] has served as a valuable guide to other spectra. Thus it is probably the simultaneous movements of electrons which account for the extreme complexity of the spectra of the halogen atoms, and of other atoms containing several loosely-bound electrons.

Only the behaviour of the valency electrons has been considered in the preceding account, but the ultimate goal of the study of line spectra, so far as it is concerned with an atomic model, is the complete assignment of orbits to all the electrons surrounding the nucleus of any atom. The pioneer attempt at a spectroscopic solution of this wider problem was made by N. Bohr [6] from considerations of both *X*-ray and optical spectra. The assignment of orbits involved calculations based on classical mechanics and the correspondence principle which have since been criticised. His conclusions have been corrected and developed, especially by J. D. Main Smith [7] and by E. C. Stoner,[8] who utilised other relevant data such as are afforded by valency regularities, *X*-ray intensities, etc. It is impossible to enlarge on their results in this Report, but it would seem that the electronic configurations of all the elements are now known with a fair degree of certainty. A general theory of complex spectra has just appeared [9] which confirms these deductions of configuration with the aid of semi-empirical rules for fixing the inner orbits. Hund has also attacked the converse problem—the prediction of spectroscopic terms from a known electronic configuration—and has predicted the constitution of the terms in the rare-earth spectra,[10] which have as yet defied empirical analysis. There are evidently good grounds for Fowler's surmise [11] that in the future the theory of spectra will be so far developed

[5] For general theory, see W. Heisenberg, *Z. Physik*, 1925, **32**, 841; *A.*, 1925, ii, 729; and F. Hund, *ibid.*, **33**, 345; *A.*, 1925, ii, 912.

[6] *Ann. Physik*, 1923, [iv], **71**, 228; *A.*, 1923, ii, 679.

[7] "Chemistry and Atomic Structure," 1925, Benn.

[8] *Phil. Mag.*, 1924, [vi], **48**, 719; *A.*, 1925, ii, 85; *ibid.*, 1925, [vi], **49**, 1289; *A.*, 1925, ii, 618.

[9] F. Hund, *loc. cit.*; and *Z. Physik*, 1925, **34**, 296; *A.*, 1925, ii, 912, 1104.

[10] *Z. Physik*, 1925, **33**, 855; *A.*, 1925, ii, 1038.

[11] Pres. Address, Brit. Assoc., Section A, 1926.

that it will become possible to calculate the positions and intensities of spectral lines with greater accuracy than they can be measured.

Line Intensities.

An experimental departure in which considerable progress has been achieved in recent years is the quantitative study of line intensities. Spectrophotometry itself is a comparatively late arrival, and spectroscopists in the past have usually been content with visual comparisons of intensity, which cannot be more than qualitative in character. L. S. Ornstein, H. B. Dorgelo, and their associates [12] have recently made accurate intensity comparisons of lines, by photographic methods, beginning with a study of doublet and triplet intensities, and extending the work to the comparison of lines in quite different spectral regions. In the latter measurements, the experimental difficulties are vastly increased, owing to the varying sensitivity of the photographic plates for different wavelengths. The principle of their measurements is the usual one of reducing the intensity of a stronger line by introducing screens of known opacity until, in an equal time of exposure, it produces the same blackening of the plate as the weaker line. In this way, all discussion of the uncertain law of blackening in relation to exposure time is avoided. The results of their measurements are of surprising simplicity. For example, the intensity ratio of the pairs in the sharp series ($2p - ms$) of the alkali metals was found [13] to be 2 : 1, within the experimental limit of 4%. For the triplets in the alkaline-earth spectra the ratios were 5 : 3 : 1, and, in general, simple integral ratios were found to govern the intensities of the components of multiplets of any complexity, both in arc- and spark-spectra. It is from results such as these that one may hope for insight into the mechanism of spectral emission, a subject which the Bohr theory has so far left very vague. The authors have developed " summation rules " from their observations, by which the intensity ratios in a group of lines can be predicted from the statistical weights of the initial and final states of the atom, which are concerned with the emission of the lines.

Results of interest of another kind have emerged from similar measurements on lines in different spectral regions. (Miss) C. E. Bleeker and I. A. Bongers [14] measured the intensity distribution among the members of the sharp and the diffuse series of rubidium and cæsium when excited in flames of different temperatures, and

[12] See reviews of methods, results, and literature : L. S. Ornstein, *Proc. Physical Soc.*, 1925, **37**, 334; H. B. Dorgelo, *Physikal. Z.*, 1925, **26**, 756; **A.**, 1926, 109.

[13] H. B. Dorgelo, *Z. Physik*, 1924, **22**, 170; *A.*, 1924, ii, 282.

[14] *Z. Physik*, 1924, **27**, 195; *A.*, 1925, ii, 77.

they found that the distribution is independent of such temperature variations. This constancy of ratio would not be expected if the lines were simple temperature emission, as their intensities should then be controlled by Kirchoff's law, and the ratio would vary with temperature. On the other hand, similar measurements have since been made on the principal-series lines [15] and the relative intensities have been found to vary with temperature in the expected direction. It is concluded that the principal series may be emitted as temperature radiation, whilst the excitation of the subordinate series is purely chemical, and is caused by the reactions proceeding in the flame.

Atomic Absorption Spectra.

When an element gives a monatomic vapour, it is possible to compare the emission and the absorption spectrum of its atoms. The two spectra are found to be closely related, but the relationship was very puzzling before the advent of the Bohr theory. No new lines appear in the absorption spectrum; indeed, it is always much simpler than the emission spectrum. Thus alkali-metal vapours only absorb wave-lengths corresponding to the lines of their "principal" series. The diffuse and the sharp series, which are quite prominent in the arc emission spectrum, do not appear in the absorption spectrum at all. The reason for this selective action of the vapour is now obvious. The valency electrons of the unexcited atoms are always bound in the innermost orbit, called the "ground" or "normal" orbit. This, of course, has characteristic principal and azimuthal quantum numbers. It is only the lines which correspond (in absorption) to a transition from this particular orbit to outer ones which can appear in the absorption spectrum. There is no mechanism by which the remainder can be absorbed. Such observations, therefore, may be used in determining the normal state of the atom, and they have frequently been employed for this purpose.[16]

It is a further deduction from the theory that if a sufficient concentration of excited atoms, with electrons in outer orbits, can be produced in the vapour, then additional series should appear in absorption. This point has been verified in several ways. For example, R. W. Wood [17] observed abnormal absorption in mercury vapour which was irradiated with an intense beam of λ 2537, the

[15] (Miss) C. E. Bleeker, *Trans. Faraday Soc.*, 1926, **21**, 479; **A.**, 657.

[16] *E.g.*, for V, Ti, Sc, H. Gieseler and W. Grotrian, *Z. Physik*, 1924, **25**, 342; *A.*, 1924, ii, 713; and for the iron group, E. v. Angerer and G. J. Joos, *Ann. Physik*, 1924, [iv], **74**, 743; *A.*, 1924, ii, 641; and K. Majumdar, *Z. Physik*, 1926, **39**, 562.

[17] *Proc. Roy. Soc.*, 1924, [*A*], **106**, 679; *A.*, 1925, ii, 3.

resonance line. The normal atoms absorbed this radiation, and, in the interval before recovery of the normal state by re-emission or collision, they were able to absorb light corresponding to other mercury lines. W. H. McCurdy [18] observed the absorption of the well-known yellow line 5875, and of 4471, etc., by excited helium. When atoms possess metastable states, it is comparatively easy to obtain the necessary concentration of excited atoms by electrical excitation. H. B. Dorgelo,[19] for example, observed such phenomena in neon, and used the time interval between the cessation of excitation and the disappearance of abnormal absorption to measure the life-periods of the metastable states. Finally, it is a deduction from Saha's theory of temperature ionisation [20] that at sufficiently high temperatures a proportion of excited atoms must be in equilibrium with the normal variety, the source of the excitation being the violent thermal agitation. At these temperatures, the absorption spectra should become richer in lines, and should include subordinate series. This phenomenon has been experimentally realised with several vapours. A. S. King [21] found that the diffuse and the sharp series of the alkali metals appeared in absorption when the vapours were heated in an electric furnace to about 2000°. Many astrophysical observations fit in with the same view. The Balmer series of hydrogen is prominent in the absorption spectrum of many classes of stars, but it has proved excessively difficult to produce the series in absorption in the laboratory.[22] The reason for the discrepancy is that the series is emitted during the return of the electron from outer orbits to the second one. The normal orbit is the first, and so atomic hydrogen as produced in the laboratory can absorb only the Lyman or ultra-violet series. On the other hand, the temperature of the stars is sufficient to secure a large enough proportion of excited atoms of the type which can absorb the Balmer series, *i.e.*, of those with the electron in the second orbit.

In addition to their line spectra, metallic vapours exhibit a very interesting continuous absorption. This begins suddenly at the limit of the series absorption and extends with decreasing intensity into the region of shorter wave-lengths. Such absorption is exhibited, for example, by sodium vapour, and it has been the subject of recent study by G. R. Harrison.[23] The same type of

[18] *Proc. Nat. Acad. Sci.*, 1926, **12**, 231; **A.**, 549.

[19] *Z. Physik*, 1925, **34**, 766; **A.**, 1926, 101.

[20] See *Ann. Report*, 1923, **20**, 5.

[21] *Astrophys J.*, 1922, **55**, 380; *A.*, 1922, ii, 810; see also N. K. Sur and R. N. Ghosh, *Phil. Mag.*, 1925, [vi], **49**, 60; *A.*, 1925, ii, 453.

[22] See, however, R. W. Wood, *Phil. Mag.*, 1926, [vii], **2**, 876; **A.**, 1069.

[23] *Physical Rev.*, 1924, **24**, 466; *A.*, 1925, ii, 5.

spectrum is also observed beyond the limit of the Balmer series in some stars such as Vega. These phenomena indicate the existence of a photo-electric effect in the vapour, for, since absorption of light of the same wave-length as the series limit is just sufficient to produce ionisation of the atom, it follows that with absorption of greater frequencies the electron is not only freed, but is ejected with an appreciable kinetic energy as well. As the absorption is continuous, ordinary quantum restrictions cannot apply to it, but attempts are being made to formulate a quantum theory of such spectra,[24] especially as parallel phenomena have proved of importance in the *X*-ray region.

Corresponding continuous emission spectra are also known, *e.g.*, for helium.[25]

Molecular Spectra.

As would be anticipated, in number and complexity molecular spectra vastly exceed those of the elements, and the theoretical treatment they have received is correspondingly incomplete, in spite of the wide interest they have aroused during the last eight years. Ever since the pioneer investigations of Hartley and Huntingdon in 1879, much attention has been paid to the spectra associated with liquids and solutions, and absorption curves have been widely, and often dangerously, quoted in discussion of the constitution of organic molecules. From the present theoretical standpoint, this work is of very little use. The only molecular spectra which can hope for an immediate theoretical interpretation are those of gases and vapours. In liquids, the influence of neighbouring molecules introduces incalculable effects on the spectra. In general, it is true, if a vapour exhibits a spectrum composed of closely-packed fine lines, then the liquid or solution will show a corresponding absorption band, shifted in position, and with the fine structure merged into a continuous absorption.[26] There is, however, no more necessary connexion between the two than there is between the absorption spectrum of sodium vapour and that of the liquid metal.

Even when the discussion is limited to the spectra of gases and vapours, the amount of available material can hardly be exaggerated. The molecules of which the spectra are known are not restricted to those which have been isolated in the laboratory. In fact, many, or most, of the better-known molecular spectra originate from

[24] J. R. Oppenheimer, *Nature*, 1926, **118**, 771.

[25] F. Paschen, *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1926, 135; **A.**, 765.

[26] Compare J. E. Purvis, *J.*, 1923, **123**, 2515; and H. G. de Laszlo, *Proc. Roy. Soc.*, 1926, [*A*], **111**, 355; **A.**, 775.

such molecules as CN, CH, NH, OH, which are incomplete according to the ordinary valency rules. Such fragmentary molecules are evidently produced in great numbers from ordinary compounds when the latter are excited by the usual methods of obtaining spectra—such as the arc and flame, or in vacuum tubes—and their life is sufficiently long to allow the emission of characteristic spectra. The observation of the spectra of more complex molecules such as those of ordinary organic compounds is, in fact, seriously restricted by this disintegrating effect of the exciting force, and as such observations are often of especial interest to chemists, the methods of overcoming the difficulty, and of obtaining the spectra of unchanged molecules, may be enumerated.

First, if a rapid stream of vapour is passed through a vacuum tube, the spectrum of the ordinary molecules will be enhanced at the expense of the spectra of the fragments, as these are given no opportunity of collecting in the tube. Schuster, many years ago, obtained the spectrum of NH_3 by this method, although a vacuum tube filled with ammonia in the ordinary way only shows the spectra of nitrogen, hydrogen, and NH. Secondly, the discharge may be so modified that its disintegrating action is minimised. W. H. McVicker, J. K. Marsh, and A. W. Stewart observed that the passage of a high-frequency, or Tesla, discharge through organic vapours, such as those of benzene and its derivatives, gave rise to spectra which were evidently those of the intact molecules. In a series of papers since 1923 they have described many such spectra.[27] The same spectra can be excited as fluorescence in the vapour, but their intensity is then too low for practical purposes. Finally, there is the method which has been most generally adopted—the observation of the absorption spectrum of the vapour. Bearing in mind the conclusions of the previous section, it might be expected that only a part of the full molecular spectrum would be obtained in this way. Spectra due to the change of the molecule from one excited state to another should not appear, but only those in which the normal state of the molecule plays a part. Actually there is usually very little difference between the absorption and the emission spectrum of a complex molecule, a conclusion reached, *e.g.*, by McVicker, Marsh, and Stewart in the investigations just quoted. One may conclude that the number of possible excited states of such molecules is strictly limited by the alternative of disintegration.

Band spectra are as characteristic of molecules as series spectra are of atoms. All evidence, both experimental and from theory, goes to show that an atom cannot emit a spectrum with band

[27] First paper, *J.*, 1923, **123**, 642; see also *Phil. Mag.*, 1924, [vi], **48**, 628; *A.*, 1925, ii, 86.

characteristics. There have certainly been recent statements to the contrary. M. Duffieux [28] asserts that measurements of the physical half-widths of the lines in the " cyanogen " bands prove the emitter to be the nitrogen atom. The width of a line, however, often exceeds that due to the simple Döppler effect. The line may, for example, be an unresolved doublet, and there are many causes of further broadening. The method can only be relied upon to give a *minimum* value for the molecular weight, and such measurements merely prove that the emitter of the " cyanogen " bands cannot be lighter than the nitrogen atom, whilst it may be much heavier. Actually, there is conclusive evidence of other kinds that both nitrogen and carbon are essential for the appearance of the spectrum, and that it must therefore be of molecular origin.

The empirical relation between the lines in a band spectrum, discovered originally by Deslandres, has been expressed in many forms, from which we may select $\nu = A + Bm + Cm^2$, where A, B, and C are constants and m takes a succession of integral values. A typical band contains a large number of lines, crowding together towards a sharp " head." This " head " may be at either the long or the short wave-length end of the band, which is said to be " degraded " in the opposite direction to the head. A complete band spectrum usually consists of several groups of such bands. This description holds for band spectra in the visible and the ultra-violet region. Bands in the infra-red may have a much simpler structure (see below). It has always been realised that the empirical expression was only an approximation, failing near the head, and J. N. Thiele,[29] as early as 1897, suggested that the head of a band could not be taken to have the same important physical significance as the limit of a series spectrum, but that its position was in some sense accidental. The quantum theory of band spectra, which has grown up during the past 8 years, has enabled their analysis to be carried much further by providing us with an insight into their constitution, and, incidentally, Thiele's supposition has been completely confirmed.

The internal energy of an atom can only change by the movement of one or more electrons from inner to outer orbits, or *vice versa*. The possible changes in a molecule are not so limited. In the discussion of band spectra, three types of energy change are recognised: (1) Changes in energy of rotation of the molecule, (2) changes in energy of vibration, and (3) changes in electronic con-

[28] *Ann. Physique*, 1925, [x], **4**, 249; *A.*, 1925, ii, 1023; *Nature*, 1926, **117**, 302; **A.**, 336.

[29] *Astrophys. J.*, 1897, **6**, 65.

figuration. The production of a line in a band spectrum in general involves changes of all three types, and the frequency of the line is determined by the algebraic sum of the three energy changes, according to the Bohr frequency condition mentioned above ($\Delta E = h\nu$), but spectra are obviously to be expected as well which correspond to molecular transitions affecting only the rotational energy, or only the rotational and vibrational energies. Such spectra are known, and it is from a consideration of these that the general theory can best be approached.

Rotation Spectra.—The quantum restriction placed upon molecular rotation is that, if the system is rotating and not emitting, the angular momentum must be an integral multiple of $h/2\pi$. This leads to the following expression for a pure rotational spectrum

$$\nu = h(2m - 1)/8\pi^2 I,$$

where I is the moment of inertia of the molecule and m takes the usual succession of integral values. Such a spectrum would consist of a number of equally-spaced lines. From non-spectroscopic evidence, I is known to be of the order of 10^{-40} for lighter molecules, and therefore such rotational spectra should appear in the far infra-red, between, say, 30 and 100 μ. This is a difficult region for experiment, but such bands have been found in the absorption spectrum of water vapour, etc. A recent investigation is that of M. Czerny [30] on the rotational spectrum of hydrogen chloride.

Rotation–Vibration Spectra.—If the molecule is treated as a simple harmonic oscillator, then the vibrational energy should only change by multiples of a definite energy unit,* which may be written $h\nu_0$. Superimposed upon this change will be alterations in the rotational energy, of the kind just mentioned, and these may be either positive or negative in sign. The result should be the appearance of a spectrum of the type

$$\nu = n\nu_0 \pm h(2m - 1)/8\pi^2 I,$$

i.e., systems of equally-spaced lines disposed about fundamental frequencies $n\nu_0$, n being a succession of integers. Actually, another factor must be taken into account. If the oscillation energy changes, then the mean distance of separation of the atomic centres will also change, and so must the value of I. Further, changes in the rotational velocity will react on the vibrational energy. The net results of these disturbances are: (1) In such spectra the lines are not quite equally spaced but close up slightly with increasing

[30] *Z. Physik*, 1925, **34**, 227; *A.*, 1925, ii, 1024.

* Leaving out of account the restriction set by the Selection Rules, which disappears with non-harmonic oscillators.

frequencies, and (2) the "over-tone" bands, corresponding to different values of n, are also not quite equally spaced.

Many such spectra are known in the near infra-red region (1—10 μ). It must be mentioned that the "zero lines," corresponding to $m = 0$, do not appear in observed spectra, and this has led to much discussion concerning the possibility of the "rotationless state."

Bands involving Electronic Changes.—The most general case of a molecular energy change is one involving, not only rotational and vibrational changes, but also the transition of a valency electron from one orbit to another. The energy associated with such a transition is of the same order as that of the atomic transitions which produce line series, and therefore "electronic" bands are usually found in the visible or ultra-violet regions. The expression for such spectra must clearly be more complex than those previously given. For one thing, the moment of inertia of the molecule will be considerably affected by electronic changes. Suppose the moment of inertia of the molecule in the initial state is I, and in the final state, after emission, it is I'. Then if $h\nu_k$ is the vibrational energy change and $h\nu_\epsilon$ the simultaneous electronic change, the lines of the band should be given by

$$\nu = \nu_\epsilon + \nu_k + \frac{h}{8\pi^2 I'} \pm \frac{2hm}{8\pi^2 I'} + \frac{h}{8\pi^2 I}\left(\frac{1}{I} - \frac{1}{I'}\right)m^2,$$

it being assumed that the selection rule holds, *viz.*, that m can change only by ± 1. This expression is of the same form as the empirical one mentioned previously, *viz.*, $\nu = A + Bm + Cm^2$, but now the three constants have been assigned a definite physical significance. It will be noted that the theory as given above would predict two series of band lines starting from a common "zero line," and corresponding, respectively, to an increase and a decrease of the rotational quantum number during emission. It has been found that the rotational quantum number may also remain constant, in which case a third series should start from the same zero line, and be given by

$$\nu = \nu_\epsilon + \nu_k + \frac{h}{8\pi^2 I}\left(\frac{1}{I} - \frac{1}{I'}\right)m^2.$$

In general, then, a band should consist of three branches:

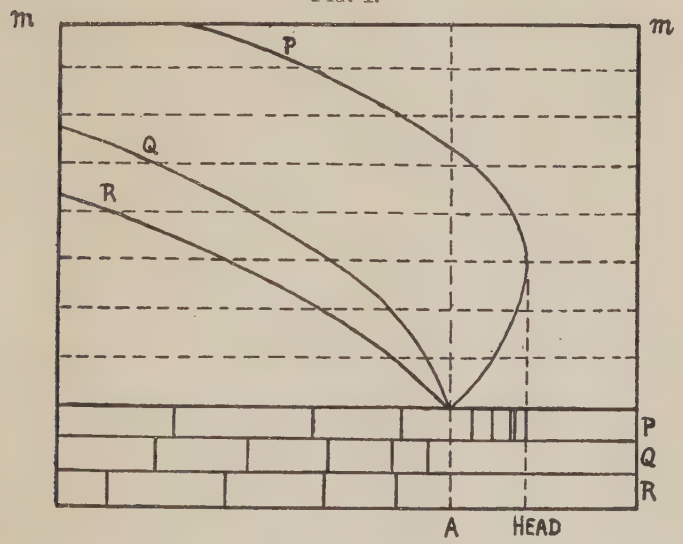
Positive (R) branch, $\nu = A + Bm + Cm^2$ [$m \longrightarrow (m - 1)$].
Zero (Q) branch, $\nu = A + Cm^2$ [$m \longrightarrow m$].
Negative (P) branch, $\nu = A - Bm + Cm^2$ [$(m - 1) \longrightarrow m$].

A graphical illustration of the relationship of the three branches is given in Fig. 1.

The concentration of lines at the head of a band is a more or less accidental result of the way in which the P-curve bends back upon itself, with increasing values of m. The important frequency, it is now realised, is not the head, but the zero line, *i.e.*, A, the constant in the band law. The zero line itself (and often neighbouring lines also, in each branch) is not developed in observed spectra.

ν_k in the formula will, in general, have several values, as there will be various vibrational states, and a band head will correspond

FIG. I.



to each. From many observations,[31] it would appear that the differences between the various values of ν_k are often nearly the same for the "electronic" bands in the ultra-violet and the visible region as for the "vibration-rotation" bands in the near infra-red.

The factors determining the intensity-distribution among the component lines in a band are still somewhat uncertain,[32] but in general the most intense line will be that associated with the most probable rotational velocity, so that the intensities should increase with the rotational quantum number (m) up to a certain maximum and then decrease gradually to a negligible value. As the temperature rises, the intensity-maximum should move to the higher members of a band, and more lines should become visible, corresponding to greater rotational velocities. Several observers have

[31] Compare E. C. C. Baly, *Phil. Mag.*, 1915, [vi], **30**, 510; *A.*, 1915, ii, 714.
[32] Compare R. Sewig, *Z. Physik*, 1926, **35**, 511; **A.**, 223.

reported such temperature-effects. R. T. Birge [33] found them for the cyanogen bands. R. S. Mulliken [34] noticed that many more lines appeared in the arc spectrum of BO and of CuI than when the same spectra were excited at ordinary temperatures by active nitrogen. J. C. McLennan, H. G. Smith, and C. A. Lea [35] found that the expected intensity changes occur in the He_2 spectrum when the vacuum tube is surrounded by liquid air or hydrogen.

The foregoing theory is the basis of the modern analysis of band spectra, but, as would be expected, the spectra of most molecules do not conform exactly with the simple theory, but exhibit peculiarities of their own. For example, it is not uncommon to find more than the theoretical three branches starting from a common zero line, and as many as twelve have occasionally been recognised. One modification of the theory which has been necessary is the introduction of " half-quantum " numbers. The expressions given above demand that the P and R branches should extrapolate into each other, as the constants are the same for both. More usually, however, the extrapolated lines of one branch fall exactly half-way between the observed lines of the other. This has led to the assumption that there are two sets of rotational states, with quantum numbers differing by $\frac{1}{2}$. The same assumption offers an explanation of the " missing lines " near the band origin.

Much interest at present attaches to the investigation of the various electronic states of molecules. Theory suggests, as we have seen, that an entire system of bands corresponds to a single electronic transition, and hence to a single line, or more generally to a single multiplet in an atomic spectrum. Analogies have accordingly been sought between the excited states of atoms and those of molecules. The band spectrum of helium provided the first evidence of such a parallel. This spectrum was discovered, and has since been analysed, by W. E. Curtis.[36] It is attributed to an unstable molecule He_2 formed in the discharge by the union of two atoms in metastable states. A. Fowler [37] observed that the heads of some of these bands were arranged in the same way as the lines in a series spectrum, and that the Rydberg constant had even its normal line-spectrum value. O. W. Richardson [38] has just disentangled six Q branches from the maze of lines in the

[33] *Astrophys. J.*, 1922, **55**, 273.

[34] *Physical Rev.*, 1925, [ii], **25**, 291; **26**, 16; *A.*, 1925, ii, 346, 833.

[35] *Proc. Roy. Soc.*, 1926, [*A*], **113**, 183.

[36] *Ibid.*, 1913, [*A*], **89**, 146; *A.*, 1913, ii, 811; *ibid.*, 1922, [*A*], **101**, 38; *A.*, 1922, ii, 330; *ibid.*, 1923, [*A*], **103**, 315; *A.*, 1923, ii, 351.

[37] *Ibid.*, 1915, [*A*], **91**, 208; *A.*, 1915, ii, 118. See also W. E. Curtis and R. G. Long, *ibid.*, 1925, [*A*], **108**, 513; *A.*, 1925, ii, 722.

[38] *Ibid.*, 1926, [*A*], **113**, 368.

secondary, or molecular, spectrum of hydrogen, the zero lines of which are all arranged according to a line-series law, with terms almost identical with the corresponding terms of the helium-doublet series, so that we have here the band analogue of the helium-doublet principal series. It is not surprising that the spectra of the two simplest possible molecules have the closest connexion with line spectra of all the band spectra so far examined, but there are indications that the electronic states of more complex molecules also tend to follow the same fundamental law.[39] R. S. Mulliken in a series of papers,[40] in which the work of other authors is also summarised, has put forward evidence for analogies between the electronic states of certain molecules and those of atoms possessing the same number of valency or outer electrons; *e.g.*, the molecules BO, CN, SiN, AlO all have one valency electron (on the "octet" theory), and just as the principal series of sodium (with its one valency electron) is composed of doublets, so these molecules give rise to double-headed bands. In the same way, triplets appear in the spectra of the alkaline earths, and triple-headed bands in the spectrum of CO, and a similar parallel can be drawn between the spectra of NO and Al.

R. Mecke [41] has observed that the terms in the hydride spectra of Zn, Cd, and Hg (*i.e.*, of ZnH, CdH, and HgH) resemble the terms in the atomic spectra of the elements immediately preceding them in the Periodic Table. Such observations may finally prove a valuable guide to the structure of molecules.

The analysis of a band spectrum already gives very varied information concerning the structure and behaviour of the molecule responsible for it. First, it gives values for the moment of inertia of the molecule, *i.e.*, for the distance between the atoms. The spacing of the lines near the band origin is, very nearly, inversely proportional to the value of I. Thus hydride spectra can often be picked out by mere inspection, as I is very small, and the spacing unusually great. Secondly, the direction in which an electronic band is degraded indicates whether the atomic centres have moved together or become more widely separated as the result of the expulsion of the electron to an outer orbit. Bands for which $I' > I$ are degraded towards the longer wave-length side, whilst if $I' < I$ they are degraded towards the ultra-violet.

The degree of stability of a molecule, again, may be indicated by its spectrum. With the brief space available for the discussion

[39] H. Sponer, *Z. Physik*, 1925, **34**, 622; **A.**, 1926, 8.

[40] *Physical Rev.*, 1925, [ii], **25**, 291; *A.*, 1925, ii, 346; *ibid.*, 1925, [ii], **26**, 561; 1926, [ii], **28**, 481; **A.**, 8, 1079.

[41] *Z. Physik*, 1926, **36**, 795; **A.**, 657.

of this point, it will perhaps be best to take a single example. A band attributed to a molecule CaH occurs at about λ 3520, and has been analysed into P and R branches. The intensity in each branch increases smoothly up to $m = 10$; the band then suddenly ends. This behaviour is most readily explained by the supposition that the molecule cannot receive a further rotational energy quantum without dissociating.[42] The absence of any associated bands in the same spectral region similarly suggests that the molecule cannot take up even a single vibrational quantum without dissociation. Curtis [43] has suggested that the He_2 spectrum is limited by similar considerations. A further discussion of the subject is given by H. Ludloff.[44]

The application of Saha's theory to the prediction of the effect of temperature on atomic absorption spectra has been mentioned in a previous section. A similar effect would be predicted for molecules sufficiently stable to possess several "excited" electronic states; *i.e.*, a percentage of the molecules should pass from the normal to the nearest excited state at sufficiently high temperatures, and new absorption bands should appear. This phenomenon has been observed with oxygen. One set of bands is present in the ultra-violet at the ordinary temperature, and others appear consecutively as the temperature is raised.[45]

The foregoing discussion has been limited to the spectra of diatomic molecules. Any more complex molecule must possess more than one effective axis of rotation, and, in addition, the possibilities of various vibrational and electronic changes also rapidly increase. The study of the spectra of such molecules becomes correspondingly difficult, although there are indications that, as has so often happened before in spectroscopic matters, the phenomena are not so complicated as a first pessimistic survey would predict. V. Henri [46] has been engaged for some years on the experimental study of the absorption spectra of organic molecules, and he has arrived at several interesting generalisations. In addition to "rotation" and "vibration-rotation" spectra, the vapours of many substances exhibit "electronic" bands. Some of these last bands have the ordinary band structure described above; others have no fine structure, but are truly continuous over a range of say, 5—10 Å. Finally, other bands of the same substance may be continuous and 100 Å. wide. Proceeding along the absorption

[42] R. S. Mulliken, *Physical Rev.*, 1925, [ii], **25**, 509; *A.*, 1925, ii, 469.

[43] *Loc. cit.* [44] *Z. Physik*, 1926, **39**, 528.

[45] C. Füchtbauer and E. Holm, *Physikal. Z.*, 1925, **26**, 345; *A.*, 1925, ii, 626.

[46] "Structure des Molecules," *Pub. de la Soc. Chim. Phys.*, XII, Hermann, 1925.

spectrum from long to short wave-lengths, there is a universal order for these types of bands : (1) fine-structure bands, (2) narrow continuous bands, (3) wide continuous bands. The interpretation set upon the narrow continuous bands, by Henri, is that the rotational energy of the molecule is not quantised during their production, whilst, to account for the bands 100 Å. wide, it is suggested that for these neither the rotational nor the vibrational, but only the electronic, energy is quantised. Henri has also analysed many of the fine-structure bands into their P, Q, and R branches, obtaining in this way the corresponding moments of inertia of the molecule. This method applied to the spectra of formaldehyde, acetone, carbonyl chloride, and other "Y-shaped" molecules has led him to conclude [47] that such molecules behave as if symmetrical, with only two effective moments of inertia, one about an axis along the stem of the Y and the other about a perpendicular axis.

As a typical example of the spectra of organic substances, we may take the naphthalene spectrum, which has recently been described by V. Henri and H. G. de Laszlo.[48] The absorption spectrum contains five distinct regions—one in the infra-red (3·25—9·81 μ), one in the visible (7140—6060 Å.), and three in the ultra-violet. Of these last three, the first (3192—2818 Å.) consists of bands with a fine structure, the second (2818—2000 Å.) of continuous bands 5—10 Å. wide, and the third (below 2000 Å.) of bands 100 Å. wide. These observations, it will be noted, are in agreement with the generalisations just mentioned. Henri deduces from these facts that there are four "excited" electronic states of the naphthalene molecule, which we may call E_1, E_2, E_3, and E_4, the "normal" state being E_0. The infra-red absorption bands are regarded as vibration-rotation bands only, whilst the other four groups represent excitation to the four "excited" states. The supposition is supported by observations on the fluorescence and cathodo-luminescence spectra of the same molecule. In position and structure, the former corresponds exactly to the transitions E_3—E_0 and E_2—E_0, and the latter to E_3—E_1 and E_2—E_1. The heads of the bands with fine structure (E_2—E_0) agree with the formula $\nu = 32455{\cdot}4 + 474{\cdot}4\,n + 203{\cdot}4\,p + 62{\cdot}6\,q$, in which n, p, and q have integral values, say + 4 to − 4. The positions of the heads are fixed by the vibrational frequencies, as we have seen, and for a diatomic molecule one of the variable terms would suffice. Here there are three, and it is concluded that there are three characteristic vibration frequencies of the naphthalene molecule concerned in the production of these bands.

[47] V. Henri and S. A. Schoń, *Compt. rend.*, 1926, **182**, 1612; **A.**, 774.
[48] *Proc. Roy. Soc.*, 1924, [*A*], **105**, 662; *A.*, 1924, ii, 513.

Spectroscopic Analysis.

In the first rush of spectroscopic discovery, the early workers in this field must have expected qualitative and quantitative analysis to be revolutionised by the new methods. Such hopes have not been realised. The spectroscope is called in as an occasional ally of the conventional chemical procedure, but in spite of a vastly increased range of instruments, and equally important improvements in technique, its application—except for a very few industrial uses—is still by no means widespread. There are, however, potentialities in spectroscopic analysis which have not been fully appreciated in recent years, owing perhaps to the general preoccupation with the physical side of spectroscopy.

Qualitative Analysis.—This side of the subject will be dismissed very briefly. The importance of the method lies in its rapidity and the certainty of detection of many elements, including most metals. Unfortunately, the sensitivity, so great for some elements, is by no means maintained for all, whilst others, notably Cl, Br, I, O, N, S, and Se, are difficult to detect at all by the usual spectroscopic procedure, although special methods could doubtless be developed. Since spectroscopic literature has become less chaotic, and trustworthy tables are now available for the identification of lines, the importance of this application is likely to increase. Its remarkable sensitivity is well illustrated by A. de Gramont's recent discovery that zinc is a constituent of all animal organisms.[49] The progress of a qualitative analysis is as follows. The material to be examined is introduced into an arc, or into a condensed spark,[50] and the spectrum photographed, generally over the wavelength range 7000—2000 Å., for which a spectrograph with a quartz train is required. A comparison spectrum,[51] often that of the iron arc or the gold spark, is cast upon the same plate. The wavelengths of the lines from the unknown material can then be found by micrometer measurements on the plate. When their wavelengths have been obtained, the lines have to be identified with known spectra. For this purpose, tables [52] are required of the more important lines of the elements, arranged in order of wavelength, and irrespective of origin.

Raies Ultimes.—In the detection of traces of an element by the

[49] *Compt. rend.*, 1920, **170**, 1037; *A.*, 1920, ii, 388.

[50] For a description of the apparatus, see papers quoted below, and F. Lowe, "Optische Messungen," Steinkopff, 1925.

[51] Tables of lines in such comparison spectra are given in Kayser's "Handbuch der Spectroscopie," Vols. V, VI, and VII, and in Twyman's "Wavelength Tables," Hilger, 1923.

[52] Kayser, "Tabelle der Hauptlinien," Springer 1926; Twyman, *op. cit.*

foregoing method, there is a further point to be remembered. Two lines that are of equal intensity in an ordinary spectrum may be very unequal when the element is present only in small quantity, and the lines which persist at the greatest dilution may be comparatively inconspicuous in the spectrum from a richer material. This fact was appreciated first by W. N. Hartley in 1884. He arranged the lines of many elements in the order of their "persistency."

More recently, de Gramont [53] has studied the same problem. Lines persisting in the spectrum, with very small quantities of the element present, he called "raies sensibles," and the last to disappear "raies ultimes." The latter, he also observed, are not always prominent in the full spectrum from an undiluted material.

The selection of these sensitive lines by Hartley and de Gramont was effected quite empirically, but modern theory has shown that their choice has a definite and important physical basis. The "persistent lines," "raies ultimes," and the closely analogous "long lines" of Lockyer are lines which are emitted during the return of electrons from some of the inner "excited states" to the innermost or "normal" state of the atom. They are therefore nearly related to—and are often identical with—the resonance lines of the elements.

This subject has been discussed by O. Laporte and W. F. Meggers [54] with the following conclusions. "Raies ultimes" are combinations of the lowest term with the first higher non-metastable term of the same series system; resonance lines are combinations of the lowest term with a term of the highest multiplicity belonging to the atom. If, therefore, the lowest term is one of the maximum multiplicity, the "raie ultime" and the resonance line will be the same.[55] Both neutral and ionised atoms provide "raies ultimes"; thus those listed by de Gramont for calcium are 3933, 3968, and 4227. The first two are due to the singly ionised calcium atom, and the third is from the neutral atom.

Quantitative Analysis.—Applications of spectroscopic observations to quantitative analysis have proved slow in development. What is needed for such purposes is some spectroscopic quantity which varies in a determinable manner with the proportion of an element present in the sample under examination. Such a quantity,

[53] There is a long series of papers by A. de Gramont on this subject in the *Compt. rend.* and elsewhere, beginning in 1907. See especially *Compt. rend.*, 1920, **171**, 1106; *A.*, 1921, ii, 73. A bibliography to 1923 and a list of lines are given by Twyman, *op. cit.*

[54] *J. Opt. Soc. Amer.*, 1925, **11**, 459; **A.**, 1926, 215.

[55] See also A. de Gramont, *Compt. rend.*, 1922, **175**, 1025; *A.*, 1923, ii, 517; W. F. Meggers and C. C. Kiess, *J. Opt. Soc. Amer.*, 1924, **9**, 372; H. N. Russell, *Astrophys. J.*, 1925, **61**, 223.

unfortunately, is not easy to find, and although several proposals have been made, the ideal solution is still lacking. The following variables have all been suggested : the intensity of the lines of the element in question, the number of the lines visible, the "length" of the lines in a spark, and the time taken for the lines of a volatile element to disappear from the spectrum.[56] The ideal general method of solving this problem would be the determination of the intensities of the characteristic lines of an element produced by a specimen when subjected to some standard excitation. This process is impracticable for several reasons. Accurate spectral-intensity determinations, although they can now be done, are still disproportionately difficult. Also there is no known law connecting the intensity of a line with the percentage of the corresponding element present in the specimen. Several more indirect methods have been proposed from time to time, and at least one of these has considerable possibilities. The first important proposal was that of N. Lockyer,[57] who observed that the "length" of a spectrum line in the spark (*i.e.*, the distance from the pole through which it spreads along the spark-gap) decreases with the proportion of the corresponding element. A comparison of the length of lines from an unknown material with the lengths of the same lines from a series of standards of known composition enabled him to make satisfactory quantitative analyses of alloys. The method is obviously too cumbrous for use. A better method was introduced by W. N. Hartley, who discovered, as stated above, that when the quantity of any element present in a material is gradually diminished to a very small value, lines due to that element successively disappear from the resulting spectrum, until only a few are left. Working with solutions of salts, he, and, later, Leonard and Pollok, tabulated the lines still observable with decreasing percentages of metal present (1·0, 0·1, 0·01, and 0·001%). By comparison of a spectrogram with these tables [58] they obtained upper and lower limits for the percentage of any element present. This method is very circumscribed, and the results may perhaps be described as "semi-quantitative," but it still serves to give a rapid indication of the proportion of any metal that may be present.

A third procedure—and the most satisfactory—has been developed by de Gramont [59] and at the Bureau of Standards by W. F. Meggers, C. C. Kiess, and F. J. Stimson.[60] The principle is

[56] C. W. Hill and G. P. Luckey, *Trans. Amer. Electrochem. Soc.*, 1917, **32**, 335; for the determination of lead in copper.

[57] *Phil. Trans.*, 1874, **164**, 479. [58] Reproduced by Twyman, *op. cit.*

[59] *Ann. Chim.*, 1909, [viii], **17**, 437; 1915, [ix], **3**, 269; *A.*, 1915, ii, 499.

[60] *Bull. Bureau of Standards*, 1922, **18**, 235; *Sci. Paper*, No. 444; *A.*, 1923, ii, 81.

to compare the intensity of lines in a spectrogram from the material under examination with their intensities in a series of spectrograms taken under the same conditions from materials of known composition. An illustration may be supplied from the paper quoted. This investigation was concerned with the analysis of alloys in which one element predominated. A very pure sample of this element was first obtained, and was used in the preparation of several graded series of alloys, each series containing one of the metals, suspected as present in the primary alloy, in the proportions 0·001, 0·01, 0·1, 1·0, and 10·0% (sometimes intermediate compositions as well). These alloys were introduced as the poles of a condensed-spark apparatus, and their spectra were successively photographed. The spectrum of the alloy under analysis was then taken with the same apparatus. By matching intensities in this last plate with those in the standards, the analysis was effected. The following table will serve as an indication of the accuracy achieved in this way. The alloys analysed were samples of boiler-plug tin.

	Spectrographic.					Chemical.			
	Cu.	Pb.	Fe.	Zn.	Ni.	Cu.	Pb.	Fe.	Zn.
No. 1.	0·1	0·1	0·005	0·001	0·001	0·08	0·10	0·03	—
No. 2.	0·6	0·05	0·1	0·07	0·001	0·62	0·04	0·04	0·06
No. 3.*	0·8	0·6	0·02	0·04	0·01	0·76	0·63	0·02	—
No. 4.*	0·6	1·0	0·01	0·15	0·01	0·65	0·98	0·042	—

* These samples also showed spectrographically, Ag 0·001, Bi 0·01%.

Analyses were made in the same way of gold used in the San Francisco mint, and of samples of platinum metals.

Such results leave no doubts of the feasibility of quantitative spectrographic analysis. The necessities for its success are the use of a standard form of apparatus, constant observing conditions, and the careful preparation of a series of comparison samples. In precision, the results, for the constituents present only in small quantity, must often surpass those obtained by gravimetric methods. It is precisely for such determinations, into which the manipulation of abnormally small precipitates, etc., must enter, that the normal methods become unsatisfactory. The spectroscope, as the above table shows, easily distinguishes between chemically similar elements which require a highly complex " wet " separation. The time taken in making a spectrographic analysis, once the standard plates have been prepared, is small in comparison with that consumed by the ordinary methods. The spectroscopic methods clearly have a greater attraction for chemists faced with a long series of routine analyses. Such restricted demands have been made upon the

methods that their limitations in many directions are still uncertain. There are, however, several papers by de Gramont dealing with applications, in addition to those to which reference has already been made. One of these [61] discusses the quantitative analysis of steels, and another contains an interesting summary of the uses of spectroscopy during the War.[62] Reference may also be made to a paper by C. Auer-Welsbach,[63] and to one by S. Judd Lewis [64] on the determination of nickel in fats.

The foregoing account has by no means exhausted the quantitative applications of the spectroscope. It is difficult, as we have seen, to make a complex molecule emit a characteristic emission spectrum, but such molecules usually possess well-marked absorption spectra, and these have been used in a variety of ways for the estimation of the corresponding compound. The well-known band spectrum of nitrogen peroxide, for example, has served for the estimation of the gas,[65] utilising the same principle as that employed for emission spectra by de Gramont, Meggers, etc., *i.e.*, comparison with a series of standard plates. The use of a spectrophotometer would render unnecessary this tedious preparation of standards. Many substances which are colourless, and therefore cannot be determined "colorimetrically," have an absorption band in the ultra-violet, and so can be estimated by these methods.

Finally, reference may be made to an ingenious method of estimating carboxyhæmoglobin, due to H. Hartridge.[66] Both hæmoglobin and carboxyhæmoglobin have a narrow absorption band in the green, but the two bands are not identical in position, although they overlap. Thus, if carbon monoxide is gradually introduced into a solution of hæmoglobin, the band appears to shift gradually towards the red until saturation is complete and the position of the carboxyhæmoglobin band has been reached. Hartridge has shown that by measuring the shift it is possible to estimate the carbon monoxide to within 1%. He has introduced an instrument—the "reversal spectroscope"—for the rapid measurement of this shift. The principle of this instrument cannot be given here, but may be found in the paper quoted above.

The Auroral Spectrum.

There are still three spectra of uncertain origin and of outstanding astrophysical interest. These originate, respectively, in nebulæ,

[61] *Compt. rend.*, 1921, **173**, 13; *A.*, 1921, ii, 474.

[62] Bull. Officiel de la Direction des Recherches et des Inventions, 1920, No. 9, 480.

[63] *Monatsh.*, 1923, **43**, 387; *A.*, 1923, ii, 247.

[64] *J. Soc. Chem. Ind.*, 1916, **35**, 663.

[65] R. Robertson and S. S. Napper, *J.*, 1907, **91**, 761.

[66] *Proc. Roy. Soc.*, 1923, [*A*], **102**, 575; *A.*, 1923, ii, 105.

in the solar corona, and in the aurora. In spite of the remarkable wave-length relationships observed by Nicholson, as early as 1912, in the first two spectra, we are still quite ignorant of the nature of the atoms—or molecules—which are responsible for them. The third problem, the origin of the auroral green line, promises to be more tractable.

The aurora typical of high latitudes is observed at heights between 90 and 470 km., and its spectrum shows the nitrogen bands, and a prominent green line at about 5577 Å. The night sky also shows a " chronic " aurora, not confined to high latitudes or to particular days, but actually increasing in intensity, for example, from the north to the south of the British Isles. Lord Rayleigh [67] has photographed the spectrum of the " chronic " aurora at different latitudes, with exposures of the order of 100 hours, and he has found that the green line is very prominent, whilst the nitrogen bands do not appear at all. The mystery is heightened by the fact that, according to theory, helium should be the main constituent of the atmosphere above 130 km., whereas the helium lines are certainly absent from the auroral light. Many hypotheses have been put forward concerning the origin of the famous green line. Passing over the suggestion of an *ad hoc* element " geocoronium," one of the first of these was the identification of the line with a prominent krypton line. More accurate wave-length determinations disposed of this somewhat tame solution. Recently, several other views have been advanced, but before these are described, an investigation may be mentioned which has, to a small measure, limited the possibilities. The " chronic " aurora is far more intense over parts of the United States than over England, and the intensity there was sufficient for Babcock [68] to photograph the green line through a Fabry–Perot étalon, with a ten-hour exposure. This investigation gave the wave-length as 5577·350 Å. with extreme certainty, and the width of the line as 0·035 Å., which is the Döppler width of a helium line at 218° K. As has been pointed out in an earlier section, this result merely fixes a minimum value for the molecular weight of the emitter. H. Bongards [69] identified the green line with a line from the blue, or enhanced, spectrum of argon. This opinion was coupled with a very speculative hypothesis as to the origin of the argon. He considered that calcium nuclei are ejected from the sun and, in their passage, either gain two electrons or lose an α-particle, and finally become argon atoms, radiating in the upper atmosphere.

[67] *Ibid.*, 1921, [*A*], **100**, 367; 1922, [*A*], **101**, 124, 312.
[68] *Astrophys. J.*, 1923, **57**, 209.
[69] *Physikal. Z.*, 1923, **24**, 279.

L. Vegard [70] obtained a remarkable phosphorescence spectrum by bombarding solid crystalline nitrogen with cathode rays. This spectrum contained broad bands in the green, one with a maximum in the neighbourhood of the auroral line. The bands, he found, became narrower as the size of the crystals diminished, and he put forward the view that 5577 was the limiting form of this spectrum, with crystals of molecular dimensions, further supposing that such crystals are present in the upper atmosphere. This theory has been strongly criticised on many grounds.[71] Finally we come to McLennan's latest investigation of this question.[72] He has obtained a green line, of wave-length 5577·35 Å., by electrical excitation, first in helium containing a little oxygen, and, later, in pure oxygen alone. The line cannot yet be correlated with any of the recognised series spectra of oxygen, but, judging from its Zeeman effect, it is of atomic and not of molecular origin. The identification of this line with the auroral one is by far the most promising solution of the problem that has been proposed. The agreement between the wave-lengths is excellent, and the oxygen spectrum is not so rich in lines that a coincidence is probable. Some explanation, of course, is still required of the prominence of this particular line in the aurora, and of the absence, or extreme faintness, of the ordinary oxygen spectrum. It must be admitted that the explanation of the spectroscopic phenomena of the aurora, even of the green line alone, is still pleasantly incomplete.

S. Barratt.

[70] *Nature*, 1924, **114**, 716; *A.*, 1924, ii, 805; *Compt. rend.*, 1925, **180**, 1084; *A.*, 1925, ii, 474.

[71] *E.g.*, J. C. McLennan and G. M. Shrum, *Proc. Roy. Soc.*, 1924, [*A*], **106**, 138; *A.*, 1924, ii, 642; and R. d'E. Atkinson, *ibid.*, 1924, [*A*], **106**, 429.

[72] J. C. McLennan and G. M. Shrum, *Proc. Roy. Soc.*, 1925, [*A*], **108**, 501; *A.*, 1925, ii, 723; J. C. McLennan, J. H. McLeod, and W. C. McQuarrie, *Nature*, 1926, **118**, 441; **A.**, 985.

INDEX OF AUTHORS' NAMES

Abderhalden, E., 181, 253.
Abel, E., 32.
Ackermann, W., 207.
Adair, 251.
Adams, E. Q., 23.
Adams, R., 110, 162.
Adler, M., 136.
Åkerlöf, G., 22, 26, 33, 35, 36.
Albrecht, W. A., 215.
Allan, J., 133, 139.
Allardt, H. G., 178, 179.
Allen, 238.
Allison, J. B., 84.
Allmand, A. J., 98.
Allpress, C. F., 80.
Alphen, J. van, 101.
Alsterberg, G., 199.
Alt, A., 203.
Aminoff, G., 275.
Andersen, A. C., 202.
Anderson, A. B., 239.
Anderson, C. T., 13.
Anderson, J. A., 214.
Andreevski, A., 53.
Andrews, D. H., 143.
Angerer, E. von, 302.
Anson, 250, 251.
Aoyama, S., 73.
Appleton, W. H., 216.
Ardagh, E. G. R., 203.
Armstrong, E. F., 74.
Arndt, F., 156, 189.
Astbury, W. T., 278, 279.
Aston, F. W., 280, 281, 282.
Athanasiu, J. A., 207.
Atkinson, H., 198.
Atkinson, R. d'E., 320.
Ato, S., 187.
Auer-Welsbach, C., 318.
Austin, H. E., 278.
Auwers, K. von, 178, 179.
Avery, 248.
Azzalin, E., 191.

Baas-Becking, L. G. M., 205.
Babcock, 319.
Bach, M., 213.
Backer, H. J., 108, 177.
Backman, P. W., 46.
Badger, R. M., 16.
Bäckström, H. L. J., 13.
Bäuerlein, K., 89.
Baines, H., 135.
Baker, H. B., 51.
Baker, J. W., 37, 115, 132.
Bakes, W. E., 212.
Bal, D. V., 213.
Balaban, I. E., 175.
Ball, G., 157.
Baly, E. C. C., 287, 309.
Barcroft, 249.
Bardwell, D. C., 292.
Barker, T. V., 107.
Barthel, C., 214.
Barton, A. W., 293.
Barton, H. A., 281.
Barton-Wright, E. C., 230.
Barzilowski, J., 120.
Basart, J., 198.
Bastings, L., 293.
Bates, 293.
Batscha, B., 293.
Bauch, 241.
Bauer, K., 158.
Baumgarten, P., 62, 156.
Bawden, A. T., 208.
Baxter, G. P., 49, 50, 51.
Baxter, W. P., 21.
Beattie, J. A., 25.
Beck, G., 69.
Becker, B., 157.
Begemann, H., 191.
Behounek, F., 294.
Beiser, A., 92.
Bell, F., 121, 122, 123, 137.
Bellerby, 237.
Benedict, 240.
Bengtsson, N., 214.
Bennewitz, K., 20.
Benrath, A., 55.
Berend, G., 82.
Berend, R., 184.
Berg, R., 190.
Berger, G., 32.
Bergmann, M., 97.
Bergstein, M., 36.
Bergstrom, F. W., 67.
Berlin, H., 89.
Bernal, J. B., 260.
Bernhauer, E., 164.
Berry, A. J., 194.

Bertho, A., 156.
Bertrand, 238.
Bessinger, 239.
Best, 238, 239.
Bickel, V. T., 201.
Bicskei, J., 189.
Biedermann, H., 66.
Biemüller, J., 266.
Bierich, 241.
Biilmann, E., 111.
Billiter, J., 44.
Bills, 254.
Biltz, H., 176, 182, 183, 184, 185.
Biltz, W., 57.
Binder, F., 190.
Binks, W., 274.
Birge, R. T., 310.
Bischoff, A., 190.
Bjerrum, N., 23, 31, 36.
Black, D. H., 287, 289.
Black, I. M. A., 87, 89.
Blarcom, H. S. van, 199.
Bleeker, (Miss) C. E., 301, 302.
Bloch, 247.
Blom, J., 189.
Blumenstock, A., 100.
Boatman, B., 215.
Bobko, E. W., 220.
Bodforss, S., 207.
Bodnár, J., 225.
Böeseken, J., 83, 106.
Böttger, K., 189.
Böttger, W., 189.
Boggio-Lera, E., 286.
Bohr, N., 300.
Bolin, I., 36.
Bomford, R. F., 33.
Bonde, J., 89.
Bone, W. A., 62.
Bongards, H., 319.
Bongers, I. A., 301.
Booth, H. S., 60, 187, 191.
Born, M., 29, 43, 261, 262, 266.
Borodin, J., 120.
Boruff, C. S., 199.
Bowen, A. R., 230.
Bracelin, P., 293.
Brackett, F. S., 297.
Bradley, A. J., 54, 274.
Bradley, W. M., 193.
Bradt, W. E., 202.
Brady, O. L., 122, 127, 139.
Bragg, (Sir) W. H., 17, 129, 264, 276.
Bragg, W. L., 17, 263, 264, 267, 270, 275, 276.
Brandt, L., 192.
Brauer, K., 202.
Braun, E., 84.
Braun, J. von, 160, 162, 180.
Brauner, B., 61.
Bray, W. C., 33.
Brennan, H., 282.
Brigl, P., 83.
Briner, E., 66.
Briscoe, H. V. A., 49, 50, 58, 283.
Bristol-Roach, B. M., 213.
Britton, H. T. S., 55, 207.
Briwul, A. A., 198.
Brode, W. R., 110.
Brodkorb, F., 54.
Brönsted, J. N., 21, 22, 26, 30, 31, 32.
Brooks, M. M., 224.
Brown, E. B., 182.
Brown, G. B., 275.
Brown, W. R., 231.
Browne, A. W., 198.
Browning, C. H., 159.
Brubaker, H. W., 199.
Bruce, 113.
Brüssoff, L., 203.
Brugger, W., 112, 113, 115, 116.
Brugsch, 240.
Brukl, A., 195.
Brumbaugh, N. J., 21.
Buchheim, R., 158.
Büchner, K., 130.
Buffington, R. M., 14, 17.
Bunker, H. J., 212.
Burd, J. S., 220.
Burger, G., 167.
Burgess, H., 40, 103, 128.
Burgess, W. G., 108, 278.
Burkhart, O., 84.
Burn, 238, 243.
Burrows, G. J., 104.
Burton, H., 141.
Buswell, A. M., 199.
Butler, A. Q., 51.
Butler, J. A. V., 24, 47.

Cabrera, 289.
Cahn, R. S., 172, 173.
Cain, J. C., 120.
Calvery, H. O., 162.
Cameron, C. N., 85.
Cameron, G. H., 294.
Campbell, R., 170.
Campbell, W. R., 203, 240.
Cannan, R. K., 226, 243.
Capelli, G., 201.
Carlier, P., 193.
Carr, E. P., 177.
Carr, F. H., 252.
Carruthers, A., 239.
Carter, J. M., 138.
Carter, J. S., 28, 37.
Cassal, A., 70.
Castan, P., 93.
Catalán, M. A., 299.
Chadwick, J., 284, 285.
Challenger, F., 130.
Chamie, (Mlle.) C., 289, 293.
Chamot, E. M., 188, 189.
Channon, 252.
Chapman, D. L., 44, 66.

Chapman, S., 263, 264.
Charlton, W., 75, 88, 89.
Charonnat, R., 104.
Chattaway, F. D., 140.
Chenault, R. L., 299.
Chibnall, A. C., 227.
Chlopin, W., 73.
Christiansen, J. A., 31, 33.
Christie, G. H., 99, 121, 122, 123.
Chuit, P., 101.
Claassen, A., 70, 271.
Claasz, M., 155.
Claisen, L., 142, 143.
Clark, W., 207.
Clark, W. M., 243.
Clarke, R., 283.
Clarke, S. G., 126, 191.
Clausen, 221.
Clinch, (Miss) P., 232.
Close, H. W., 34.
Clutterbuck, P. W., 98.
Coffey, S., 141.
Cofman, V., 135.
Coghill, R. D., 182.
Cohen, B., 243.
Cohen, J. B., 159.
Cole, H. I., 188.
Colin, H., 221, 228.
Collenberg, O., 206.
Collison, R. C., 215.
Colvin, J., 27, 34.
Compton, A. H., 271, 272.
Conant, 251.
Condon, E., 291.
Conn, R. J., 215.
Conrad, M., 161.
Conrath, P., 192.
Consigny, J., 291.
Coode-Adams, W. R. C., 42.
Cooper, C. J. A., 87.
Cooper, W. C., 50.
Corran, J. W., 27.
Costa, J. L., 281.
Coulson, E. A., 140.
Coward, 252.
Cox, R. R. S., 20.
Cray, F. M., 200.
Crepaz, E., 188.
Crighton, A., 221.
Crookes, S. I., 182.
Cruikshank, E. M., 221.
Csonka, F. A., 227.
Curie, (Mlle.) I., 289, 291, 292, 293.
Curie, (Mme.) M., 290.
Curtis, W. E., 310, 312.
Curtiss, L. F., 288, 289, 293.
Curtius, T., 156.
Cutter, J. O., 40, 416.
Czerny, M., 307.
Czerny, W., 100.

Dachselt, E., 204, 207.
Dakin, 240.
Dale, 238, 239.
Damiens, A., 61.
Daniels, F., 66.
Darmois, E., 41.
Darwin, C. G., 267.
Davey, W. P., 194.
Davies, (Miss) A. C., 65, 287.
Davis, A. R., 223.
Dawson, H. M., 37.
Day, H. A., 198.
Dean, N. C., 37.
De Barros, D., 282.
De Boer, J. H., 64, 65, 188, 198.
De Broglie, M., 289, 290.
De Bruyn, B. R., 132.
Debye, P., 28, 144, 285.
Decker, H., 164.
Deckert, 100.
De Cugnac, A., 228.
De Gramont, A., 314, 315, 316, 318.
De Jongh, 237.
De la Peña, P., 194.
De Laszlo, H. G., 304, 313.
Delaville, M., 193.
Delbanco, A., 32.
De Liefde, W., 70.
De Mallemann, R., 43.
Demjanov, N. J., 112.
Denigès, G., 187.
Dennett, H. G., 122, 137.
Dennis, L. M., 63.
Dent, (Miss) B. M., 263, 264.
Derlon, G. K. H., 112.
De Smedt, J., 273.
D'Espine, J., 288, 289.
Deuel, 240.
Deuticke, 242.
Deutsch, 241.
De Vries, T., 15.
De Wolff, C. J., 87.
Diaz, F. O., 193.
Diaz de Rada, F., 187.
Dickhäuser, E., 84.
Dickson, E. C. S., 274.
Diekmann, H., 35.
Dillon, T., 283.
Dimond, D. W., 27.
Dimroth, O., 141.
Diwald, J., 230.
Dixon, A. L., 15.
Dobbrow, M. A., 177.
Dobroserdov, D., 195, 196.
Dobson, G. M. B., 205.
Doebner, O., 160.
Dörsam, H., 68.
Doisy, 237.
Dolejšek, V., 72.
Domontovitch, M., 220.
Donath, E., 190.
Donde, A., 45.
Dopter, P. L., 215.
Dorcas, M. J., 224.
Dore, W. H., 228.

Dorée, C., 230.
Dorgelo, H. B., 301, 303.
Dox, A. W., 183.
Doyle, J., 232.
Drew, 78.
Drophy, D. H., 194.
Druce, J. G. F., 72.
Drummond, A. M., 163.
Drummond, J. C., 252, 253.
Dschu, G. L., 167.
Duane, W., 269.
Dubois, O. E., 200.
Dudley, H. W., 243, 248, 255, 256.
Duffieux, M., 66, 306.
Duhme, E., 287.
Duin, C. F. van, 173.
Dunker, E., 159.
Dunlop, J. G. H., 102.
Dunnicliff, H. B., 69, 191.
Dureuil, E., 205.

Eastman, E. D., 12, 14, 17.
Ebert, L., 33, 140, 147.
Edmondson, W., 19.
Egerton, A. C. G., 18, 19.
Eggleston, J. A., 203.
Eichler, T., 164.
Eigenberger, E., 198.
Ehrenfest, P., 16.
Eilert, A., 57.
Einstein, A., 19, 20.
Ekkert, L., 202.
Elek, A., 202.
Eller, 210.
Ellingworth, S., 159.
Elliott, W., 221.
Ellis, C. D., 288, 290.
Elsey, H. M., 52.
Embden, 242.
Emeléus, H. J., 68.
England, E. H., 203.
Enke, F., 212.
Ephraim, F., 69, 71.
Epstein, H., 164.
Erbacher, O., 60.
Erben, F. X., 162.
Erdmann, V., 196.
Errera, J., 146, 148, 292.
Escher, K., 110, 150.
Essers, H., 55.
Estill, H. W., 187.
Ettel, V., 204.
Ettisch, G., 44.
Eucken, A., 19, 20.
Euler, H. von, 36, 37, 38, 86, 87, 252.
Evans, B. S., 191.
Ewald, P. P., 258, 267.
Ewbank, E. K., 127.

Fairweather, D. A., 102.
Faivret, T., 154.
Fales, H. A., 33.
Falk, K. G., 155.
Fast, J. D., 64.
Faulkner, I. J., 38, 86, 103.
Fear, C. M., 99.
Fearon, 252.
Feist, K., 167.
Fellenberg, von, 230.
Ferenczy, J., 225.
Fernandes, L., 61, 188.
Ferriss, C. V., 122.
Fichter, F., 71, 136.
Field, J., 205.
Fieser, L. F., 178.
Fife, J. M., 216.
Fikentscher, H., 60.
Finkelstein, (Mlle.) M., 165.
Fischer, E., 75.
Fischer, E. J., 186.
Fischer, F., 209.
Fischer, H., 151, 152, 249.
Fischer, W. M., 193.
Fleury, P., 183.
Flürscheim, B., 130, 133.
Foerster, F., 69.
Fogg, H. C., 194.
Foote, H. W., 193.
Forster, M. O., 128.
Forsyth, R., 136, 140, 158, 175, 181.
Fosse, R., 227.
Foulk, C. W., 208.
Fournier, G., 293.
Fowler, A., 297, 300, 310.
Fowler, R. H., 19, 291.
Fowles, G., 55.
Francis, A. W., 134, 135, 143, 192.
Fraser, R. P., 62.
Freitag, K., 293.
French, H. E., 201, 202.
Frerichs, G., 167.
Frese, E., 179.
Fretwurst, F., 128.
Freudenberg, K., 81, 82, 84, 201, 230.
Freund, M., 158.
Freundler, P., 193.
Freundlich, H., 44.
Fricke, R., 56.
Fridli, R., 191, 192.
Fried, F., 19, 20.
Friedländer, P., 154.
Friedrich, A., 230.
Friedrich, H., 115.
Fritzmann, E., 73.
Frivold, O. E., 21.
Frommer, S., 68.
Frumkin, A., 44, 45, 46, 47.
Fryling, C. F., 36.
Fuchs, W., 212, 230.
Füchtbauer, C., 312.
Fürth, O., 203.
Funck, A. D., 195.
Funk, 238.

Gadamer, J., 166, 172.
Gans, R., 144.
Garby, C. D., 203.
Garrett, M. W., 247, 286.
Garrett, W. H., 34.
Garrison, A., 46.
Gaspar y Arnal, T., 187, 189.
Gatewood, E. S., 185.
Gauerke, C. G., 201.
Geiger, H., 291.
Geilmann, W., 186.
Georg, A., 89.
Georgievic, 155.
Gericke, W. F., 223, 224.
Germann, A. F. O., 60.
Ghosh, R. N., 303.
Giauque, W. F., 13.
Gibbs, R. E., 243, 276.
Gibson, C. S., 160.
Gibson, G. E., 11, 12, 13, 15.
Gibson, K. S., 205.
Gieseler, H., 302.
Gilbert, E., 221.
Gilbert, H. W., 46.
Gilman, E., 177.
Gimingham, C. T., 197.
Ginsburg, J. M., 226.
Gläser, H., 68.
Glasstone, S., 27.
Glawe, H., 102.
Gleditsch, (Mlle.) E., 283, 289.
Godbole, N. N., 100.
Godden, W., 221.
Goebel, 248.
Götze, R., 297.
Goldschmidt, F., 286.
Goldschmidt, V. M., 277.
Goldstein, R. F., 127.
Goll, O., 180.
Golubev, B. A., 220.
González, A., 99.
Gooch, F. A., 197.
Goodman, R. A., 66.
Gordon, 249.
Gorr, G., 98.
Goss, F. R., 101, 130.
Goto, K., 171.
Gotts, R. A., 103, 105, 128.
Gottschalk, A., 225.
Goudsmit, S., 299.
Gounder, A., 151.
Gouy, G., 44.
Gradenwitz, F., 57.
Grafe, V., 231.
Graffunder, W., 146.
Grandsire, A., 221.
Grassl, G., 191.
Gray, F., 43.
Gray, H. le B., 97.
Greeff, A., 197.
Greeske, H., 102.
Griggs, M. A., 228.
Grignard, V., 70.
Grigorjev, P., 204.
Grimm, H. G., 266.
Gröhler, K., 72.
Grosskopf, W., 209.
Grotrian, W., 302.
Grover, C. E., 227.
Grube, G., 34, 36.
Gruber, H., 160.
Grün, A., 100, 101, 203.
Grüneisen, E., 14.
Grünthal, E., 69.
Grundherr, G. E. von, 91.
Güntelberg, E., 22.
Gulbransen, R., 159.
Gulland, J. M., 172.
Gurevitsch, W. G., 31.
Gurney, R. W., 289, 291.
Guth, E., 285.
Guy, W. G., 294.
Guyot, O., 190.
Gyemant, A., 29, 44.

Haas, P., 225.
Haas, R., 181.
Haase, W., 217, 286.
Haber, F., 44, 286.
Hachl, A., 132.
Händler, W., 68.
Hahn, D. A., 177.
Hahn, F. L., 72, 196.
Hahn, O., 288, 293.
Halbig, P., 152.
Hall, L. P., 51, 283.
Haller, A., 41.
Hamano, 254.
Hamid, M. A., 193.
Hammick, D. L., 33.
Hammond, F., 141.
Hanhart, W., 130.
Hanika, F., 200.
Hanisch, H., 184.
Hanke, M. T., 204.
Hansen, W., 153.
Hanuš, J., 194.
Harden, L. J., 221.
Hardmeier, W., 285.
Hardy, F., 221.
Hargreaves, G. W., 201.
Hariharan, K. V., 160.
Harington, 234, 235.
Harkins, W. D., 50, 283, 294.
Harned, H. S., 21, 22, 26, 33.
Harnisch, C., 201.
Harnwell, G. P., 281.
Harper, H. J., 214, 215.
Harris, E. R., 27.
Harris, J. E., 60.
Harrison, D. N., 205.
Harrison, G. A., 247.
Harrison, G. R., 303.
Harrison, P. W. B., 107, 126.
Hart, 237.

Hartley, H., 24.
Hartley, W. N., 316.
Hartmann, 237.
Hartridge, H., 318.
Hartung, E. J., 55.
Hauser, E. A., 277.
Havestadt, L., 56.
Havighurst, R. J., 269, 270, 271, 272.
Hawley, F. G., 197.
Haworth, R. D., 163, 166, 167, 168, 169, 170, 171.
Haworth, W. N., 75, 76, 78, 80, 84, 87, 88, 89, 90, 91.
Hay, K. G., 200.
Hecht, O., 191.
Heckmann, G., 266.
Heczko, T., 195.
Hedström, I., 86.
Hedvall, I. A., 57.
Heidelberger, 248.
Heilbron, 255.
Heinzler, J., 105.
Heisenberg, W., 262, 300.
Helfer, L., 162.
Helferich, B., 85, 89.
Heller, G., 152, 158, 159.
Heller, R., 191.
Helms, H. B., 216.
Henderson, G. H., 292.
Hendricks, S. B., 273, 275.
Henri, V., 292, 312, 313.
Hentschel, H., 98.
Hepburn, 240.
Herbst, H., 61.
Herzfeld, K. F., 17, 44, 258.
Herzog, R. O., 277.
Herzog, W., 204.
Hess, H., 201, 230.
Hess, K., 95.
Hess, V. F., 294.
Hess, W. R., 253, 254.
Hetterschij, C. W. G., 207.
Hettich, A., 258.
Heuser, E., 97.
Heusler, O., 71.
Heyrovský, J., 72, 206.
Hibbard, P. L., 196, 223.
Hickinbottom, W. J., 107.
Hicks, H. C., 15, 16.
Hicks, J. S., 205.
Hilditch, T. P., 99.
Hill, A. E., 55.
Hill, C. W., 316.
Hill, E. L., 201.
Hill, R., 249, 250.
Hill, T. G., 225.
Hinchy, V. M., 283.
Hinkel, L. E., 156.
Hinshelwood, C. N., 36.
Hirsch, P., 208.
Hirsch-Kauffmann, 242.
Hirst, C. T., 109.
Hirst, E. L., 78, 80, 88, 90.
Hirst, H. S., 67.
Hixon, R. M., 84.
Hoagland, D. R., 219, 223.
Hock, A., 207.
Hodgson, H. H., 137.
Höjendahl, K., 147.
Hönigschmid, O., 283, 286.
Hoet, J. P., 238, 239, 242.
Hofer, K., 57.
Hoffman, W. F., 228.
Hoffmann, G., 294.
Hoffmann, H., 158, 159.
Holben, F. J., 212.
Holbøll, 239, 240.
Holde, D., 100.
Holden, H. F., 249.
Holderness, A., 121, 123.
Holleman, A. F., 132, 138, 141, 176.
Hollmann, H., 178.
Holluta, J., 32.
Holm, E., 312.
Holmberg, B., 111.
Holmes, A., 291.
Holmes, B. E., 241.
Holmes, E., 100.
Holmes, E. L., 130, 138.
Holter, H., 166.
Holton, W. B., 60.
Honneyman, W., 228.
Hope, E., 171.
Hopkins, B. S., 61.
Hopkins, (Sir) F. G., 245.
Hoppmann, H., 153.
Hori, T., 282.
Horlein, 173.
Horsters, 240.
Horton, F., 65, 287.
Hoskins, C. R., 37.
Hudig, J., 207.
Hudson, C. S., 39, 78, 90.
Hückel, E., 21.
Hückel, W., 115, 162.
Hüttig, G. F., 54.
Huffman, H. M., 13, 14.
Humpert, K., 71.
Humphries, J. E., 159.
Hund, F., 265, 300.
Hunter, H., 39, 40.
Hunter, R. F., 182.
Hurst, (Miss) W. G., 161.
Hutchison, W. K., 33.
Huttner, K., 61.
Hynd, A., 85.

Ihrig, H. K., 109.
Ing, H. R., 130.
Ingham, G., 220.
Ingold, C. K., 37, 101, 130, 132, 134, 135, 138.
Ingold, (Mrs.) E. H., 132, 134, 135, 138.
Inoko, S., 190.

Ipatiev, V., 53, 68.
Irvine, (Sir), J. C., 81, 82, 87, 89, 90, 94, 97.
Irving, 240.
Irwin, M., 224.
Isajev, J. V., 89.
Isler, 237.
Isnard, E., 194.
Itagaki, T., 228.
Ives, H. E., 282.

Jabłczyński, K., 29, 64.
Jacob, P., 39.
Jacobsen, J. C., 292.
Jaeger, F. M., 50, 72.
Jaenicke, J., 286.
Jahn, R., 92.
Jajte, S., 190.
James, C., 194.
James, C. W., 121.
James, G. M., 26.
James, R. W., 267, 271, 274.
Janke, A., 200.
Jeans, J. H., 295.
Jeffrey, G. H., 51.
Jellinek, K., 20.
Jenkins, C. H. M., 58.
Jenkins, F. A., 284.
Jensen, B. M., 202.
Jevons, W., 284.
Jilek, A., 194, 204.
Job, A., 70.
Jodidi, S. L., 204.
Johnson, J. R., 201.
Johnson, T. B., 177, 182.
Johnstin, R., 228.
Johnston, J., 143.
Johnston, W. W., 216.
Jones, C. M., 33, 34.
Jones, D. B., 227.
Jones, E. C., 27.
Jones, G. G., 39, 85.
Jones, H. O., 102.
Joos, G. J., 302.
Jordan, 237.
Jürgens, J., 141.
Julius, (Mlle.) A., 83.
Jung, H., 141.
Jungermann, C., 227.
Justh, R., 62.

Kämpf, A., 120.
Kalb, L., 152.
Kall, G. A., 105.
Kalle, 241.
Kallmann, H., 272.
Kametaka, T., 113.
Kamm, 255.
Karlsson, K. G., 37.
Karlsson, S., 252.
Karrer, P., 110, 150.
Karssen, A., 65.
Karwat, E., 20.
Kaspar, E., 71.
Kast, H., 200.
Kasten, E., 95.
Katz, J. R., 277.
Kaufler, F., 120.
Kaul, L., 287.
Kay, F. W., 115.
Kayser, 314.
Keesom, W. H., 52, 273.
Keilin, 250, 251.
Kelley, K. K., 13.
Kemmerer, G., 192.
Kemper, W., 155.
Kendall, E. C., 152, 234, 235.
Kenner, J., 120, 121, 125, 141.
Kenrick, F. B., 45.
Kenyon, J., 107, 110, 111, 121, 122, 123, 126, 137.
Keppler, H., 83, 154.
Kermack, 240.
Kiess, C. C., 315, 316.
Kiliani, H., 84.
Kilpatrick, M., 32, 34, 36.
King, A. S., 303.
King, C. V., 32.
King, F. E., 71.
King, H., 156, 175.
King, H. S., 51, 283.
Kipping, F. B., 181
Kirsch, A., 156.
Kirsch, G., 285.
Kitasato, Z., 167.
Klarer, J., 151, 249.
Klason, P., 210.
Kleeman, R. D., 46.
Klein, G., 225.
Klein, H., 185.
Klein, W., 89.
Klemm, W., 183.
Klement, R., 72.
Klenk, E., 100.
Knehe, E., 97.
Knorr, L., 161, 173.
Knowles, H. B., 194.
Koblic, O., 294.
Kobayashi, M., 197.
Koch, E., 217.
Kodama, 247.
Köhl, A., 197, 198.
Köhler, T., 182.
König, F., 195.
König, J., 73.
König, W., 158.
Königs, E., 157.
Köszegi, D., 199.
Koets, P., 72.
Koller, G., 120.
Koller, I., 82.
Kolodny, S., 84.
Kolthoff, I. M., 189, 191, 199, 200, 204, 205.
Konarzewski, J., 56.

Konowalowa, R. A., 182.
Konrad, E., 67.
Koppova, B., 204.
Kornfeld, H., 264.
Korschun, G., 150.
Korsunski, M., 72.
Kosche, W., 85.
Kossel, A., 203.
Kotake, M., 172.
Koulen, K., 173.
Kraub, H., 63.
Kraut, H., 60.
Kremers, F., 142.
Kremers, H. C., 60.
Krezil, F., 101.
Krishnamurti, S., 191.
Kronman, J., 44.
Kropacsy, S., 200.
Kühling, H. E., 178.
Kürschner, K., 196, 202, 212.
Kuhn, R., 39, 91, 93, 123.
Kulvarskaya, R., 45.
Kummer, M. von, 126.
Kunsman, C. H., 281.
Kunz, A., 90.
Kunze, K., 138.
Kuylman, H. A., 191.

Labes, R., 44.
Lachs, H., 44.
Ladenburg, R., 18.
Laidlaw, 248.
Lambie, 240.
La Mer, V. K., 30.
Landé, A., 43.
Lang, I., 60.
Lang, N., 165.
Lang, R., 208.
Lange, E., 207.
Lange, F., 13.
Lange, W., 62.
Laporte, O., 315.
Lapp, C. J., 61.
Lapworth, A., 36, 134.
Laqueur, 237.
Lassieur, A., 192.
Latimer, W. M., 12, 13, 14, 15, 17, 29.
Lawson, R. W., 291.
Lea, C. A., 310.
Le Boucher, L., 193.
Lebeau, P., 61.
Leduc, A., 216.
Lee, J. van der, 152.
Lefèvre, L., 154.
Le Fèvre, R. J. W., 122, 123, 125, 137.
Lehnartz, 242.
Leibowitz, J., 89, 93, 94, 95, 96.
Leitch, (Miss), G. C., 89.
Lemkin, W., 36.
Lemoigne, M., 215.
Lennard-Jones, J. E., 261, 263, 264, 266.
Leonard, 316.
Lesser, 239.
Lessing, R., 194.
Levene, P. A., 77, 81, 85, 231.
Lewis, B., 71.
Lewis, G. N., 11, 12, 15, 24, 144.
Lewis, N. B., 56.
Lewis, S. J., 318.
Lewis, W. C. McC., 27, 33, 34.
Lichtenstein, W. J., 56.
Liebreich, E., 48.
Lifschitz, I., 104, 155.
Limpach, L., 161.
Limpächer, R., 203.
Linckh, E., 72.
Lind, S. C., 292.
Lindberg, S., 209.
Linderström-Lang, K., 28.
Lindner, J., 160.
Line, J., 223.
Linnell, W. H., 91.
Livingston, R. S., 33.
Ljubavin, H., 157.
Lobinger, K., 63.
Lockyer, N., 316.
Loeb, L., 291.
Loew, O., 227.
Lohmann, 242.
Long, E. R., 248.
Long, R. G., 310.
Longchambon, L., 42.
Looney, J. M., 204.
Loring, F. H., 72.
Lotter, P., 136.
Lotz, A., 287.
Lourie, H., 155.
Lowe, F., 314.
Lowry, T. M., 37, 38, 39, 40, 41, 42, 85, 86, 103, 106, 107, 128, 150, 155.
Lucas, H. J., 134, 138.
Lucas, R., 41, 42.
Lucasse, W. W., 21.
Luckey, G. P., 316.
Ludlam, A. E., 264.
Ludloff, H., 312.
Ludwig, O., 216, 217.
Lüde, K. von, 20.
Lukas, J., 194, 206.
Lundell, G. E. F., 194.
Lundsgaard, 239.
Lyon, T. L., 214.
Lyons, R. E., 202.

McAulay, J., 28.
McBain, J. W., 200.
Macbeth, A. K., 78.
McClennan, J. C., 273.
McCurdy, W. H., 303.
McDonald, F. G., 254.
Macdonald, J., 94.
MacDougal, 232.

McEwen, W. L., 201.
McHargue, J. S., 221.
Mâchebœuf, 238.
McHugh, G. P., 122.
MacInnes, D. A., 24, 25.
McKee, M. C., 228.
McKeehan, L. W., 275.
McKenzie, A., 110, 111.
MacKenzie, B. F., 152.
McKeown, A., 28.
McLean, F. T., 221.
McLennan, J. C., 310, 320.
McLeod, J. H., 320.
McMath, A. M., 108.
McMillan, A., 163.
McOwan, G., 81, 91.
McQuarrie, W. C., 320.
McVicker, W. H., 305.
Madel, W. R., 156.
Madelung, W., 154.
Magistris, H., 231.
Maier, C. G., 13.
Majumdar, K., 302.
Malaprade, L., 207.
Malherbe, D. F. du T., 141.
Mali, S. B., 70.
Malkin, T., 278.
Malquori, G., 57.
Maltby, J. G., 87.
Manchot, W., 72, 73, 191.
Mandel, 240.
Manley, J. J., 205.
Mann, C. E. T., 221.
Mann, F. G., 109.
Mannich, C., 157.
Maracineanu, (Mlle.) S., 294.
Marchal, (Mlle.) G., 57.
Marcusson, J., 212.
Mark, H., 257, 272, 273, 277.
Marks, H. P., 238, 239, 242, 243.
Marrian, 253.
Marsh, J. K., 305.
Marshall, P. G., 134.
Martin, G., 63.
Martin, J. C., 219.
Martinet, N., 132.
Martini, A., 32.
Marvel, C. S., 201.
Mason, C. W., 189.
Mason, E. H., 240.
Mason, F. A., 158.
Matthias, F., 286.
Matula, M., 198.
Maulwurf, O., 162.
Maurer, K., 84.
Mauss, H., 178.
Maw, W., 84.
Max, F., 184.
Maxymowicz, W., 191, 195.
Mayer, H., 112.
Mayr, C., 189.
Mecke, R., 311.
Meckenstock, H., 55.
Meggers, W. F., 315, 316.
Mehta, M. M., 230.
Meier, H. A., 72.
Meijer, W., 177.
Meiner, C., 66.
Meisenheimer, J., 102, 126, 158, 159.
Meitner, (Frl.) L., 288, 293.
Mellanby, J., 237.
Mellet, R., 190.
Ménager, (Mlle.) Y., 193.
Mendel, 241.
Menon, K. N., 160.
Menzer, G., 276.
Menzies, A. W., 283.
Menzies, R. C., 99.
Merck, F., 61.
Merton, 284.
Messe, W., 192.
Meulen, H. ter, 202.
Meulenhoff, J., 106.
Meurice, R., 187.
Meyer, G. M., 85.
Meyer, H., 157.
Meyer, J., 71, 72, 136, 188.
Meyer, L., 217.
Meyerhof, 242, 245.
Michaelis, A., 130.
Michler, W., 120.
Micklethwait, (Miss) F. M. G., 130.
Middleton, A. R., 188.
Miethe, A., 285.
Mika, J., 187.
Miller, F. W., 55.
Miller, W. von, 160.
Millikan, R. A., 294.
Mills, W. H., 102, 103, 105, 124, 128, 158.
Milobedzki, T., 190.
Mindalev, L., 187.
Minkowski, R., 18.
Mirsky, 250, 251.
Mitchell, A. C. G., 15, 16.
Mohrschulz, W., 98.
Moldenhauer, W., 68, 206.
Mook, H. W., 108.
Moore, 252.
Moran, T., 34.
Morand, M., 282.
Morgan, G. T., 100, 107, 109, 110, 129, 130, 279.
Morrell, J. C., 33.
Morton, 255.
Moschini, 240.
Moser, L., 191, 200.
Mosettig, E., 166.
Mouromtsev, B. A., 53.
Moyse, H. W., 138.
Muchin, G. E., 31.
Mühlendahl, E. von, 57.
Müller, E., 98, 192, 204, 207.
Müller, F., 206.
Müller, Friedrich, 73.
Müller, H., 54.

Müller, K., 183.
Mulliken, R. S., 284, 310, 311, 312.
Muret, P., 70.
Murlin, 238.
Murphy, J. C., 227.
Myrbäck, 252.
Myssovski, L., 294.

Nachmann, M., 192.
Nachtwey, P., 156, 189.
Nagaoka, H., 282, 286.
Nair, S. U., 161.
Nakamura, Y., 228.
Nakazono, T., 190, 195.
Nametkin, S., 203.
Napper, S. S., 318.
Nash, A. W., 230.
Navarro, E., 202.
Neale, S. M., 96.
Neber, P. W., 154.
Negelein, 241.
Neller, J. R., 216.
Nelson, J. M., 155.
Nenitzescu, C., 151, 152.
Nernst, W., 20, 24.
Nestle, K. T., 73.
Neuberg, C., 98, 225.
Neumaerker, J., 128.
Neville, H. A., 56.
Newitt, D. M., 62.
Nicholson, V. S., 75.
Nicloux, 251.
Niehaus, H., 55.
Nijhawan, S. D., 69.
Nikolajev, W., 68.
Nimkar, V. K., 140, 175.
Noller, C. R., 162.
Nonhebel, G., 24.
Norris, F. W., 228.
Norström, E., 57.
Norton, J. T., 205.
Noyes, A. A., 25.
Nugent, R. L., 187.

Oberlin, M., 172.
Obrutshewa, A., 47.
Odén, S., 209.
O'Dwyer, M. H., 231.
Ölander, A., 37, 38, 87.
Ogburn, S. C., jun., 189.
Ohle, H., 82, 83, 84.
Okuda, Y., 204.
Oldham, J. W. H., 85.
Olsen, R., 34, 35.
Onnes, H. K., 52.
Oparina, (Mlle.) M. P., 157.
Oppenheimer, J. R., 304.
Orndorff, W. R., 63.
Ornstein, L. S., 301.
Orr, J. B., 221.
Orthmann, W., 24.
Oseen, C. W., 43.
Ost, H., 89.
Osterberg, A. E., 152.
Osterhout, W. J. V., 224.
O'Sullivan, J. B., 207.
Ott, E., 96.
Ott, H., 276.
Oxford, A. E., 134, 139.

Padovani, C., 68.
Page, H. J., 197.
Palkin, S., 205.
Paneth, F., 52, 287.
Pantschenko, G. A., 188.
Park, B., 192.
Parker, F. W., 219, 220.
Parkes, 237.
Parks, G. S., 12, 13.
Partington, J. R., 71.
Paschen, F., 287, 304.
Pastak, I. A., 144.
Pate, W. W., 220.
Patrick, W. A., 46.
Patterson, J., 81, 82, 90.
Patterson, T. R., 144.
Patterson, T. S., 41.
Pauchard, M. E., 204.
Paul, B. K., 72.
Paul, J. R., 239.
Pauling, L., 12, 273, 275.
Pawletta, A., 188.
Peachey, 108.
Peat, S., 75, 76, 87, 88, 89.
Pedersen, K., 32.
Pellens, L., 67.
Pennycuick, S. W., 33.
Perkin, W. H., jun, 152, 163, 166, 167, 168, 169, 170, 171.
Perpérot, H., 67.
Perrette, (Mlle.) B., 284.
Peters, K., 52, 287.
Peterson, J. B., 201.
Petrich, W., 72.
Pettersson, H., 285.
Pfeiffer, M., 115, 116.
Philip, J. C., 27.
Philippi, E., 162.
Philippovich, A. von, 212.
Philipps, K., 293.
Phillips, H., 106, 107, 110, 111, 126.
Piaux, L., 185.
Piccard, A., 288.
Pickard, R. H., 40.
Pictet, A., 89, 92, 93, 165.
Pilley, J. E. G., 282.
Pink, H. S., 166.
Pinkus, G., 57.
Piper, S. H., 278.
Pirschle, K., 225.
Pisani, F., 197.
Pitts, C. R., 46.
Piutti, A., 286.

Planck, M., 20.
Plato, W., 105, 129.
Pohland, C., 273.
Pohland, E., 59, 191.
Pohlmeyer, W., 289.
Polgar, N., 164.
Polland, B., 72.
Pollok, 316.
Pope, (Sir) W. J., 108, 109, 181.
Porter, C. W., 109.
Porter, L. E., 200.
Posner, T., 155.
Pound, A., 27.
Prandtl, W., 61.
Price, 252.
Priebs, B., 132.
Pringsheim, H., 84, 89, 92, 93, 94, 95, 96.
Pschorr, 171.
Pucher, G. W., 198.
Pugh, W., 63.
Purvis, J. E., 304.
Pyman, F. L., 136, 140, 158, 175, 181.

Quastel, 245.
Quick, W. G. E., 139.
Quietensky, H., 167.
Quig, J. B., 63.

Ralls, 237.
Ram, K., 191.
Randall, J. T., 271.
Randall, M., 24.
Rankin, J., 163, 171.
Raper, H. S., 98, 247.
Raper, R., 105, 158.
Raquet, D., 187.
Rath, 158.
Rawlins, F. I. G., 20.
Rây, P., 71.
Ray, S. N., 71.
Rayleigh (Lord), 319.
Read, J., 108, 181.
Read, J. B., 106, 131.
Reeve, L., 98.
Reich, H., 162.
Reiche, F., 16.
Reichstein, S., 45.
Reichstein, T., 201.
Reihlen, H., 57, 73, 104, 105.
Reinicke, R., 282.
Reinitzer, B., 192.
Reissert, A., 153.
Remy, H., 189.
Reverey, G., 102.
Rice, A. C., 194.
Rice, F. O., 36.
Rice, O. K., 44, 47.
Richards, E. M., 37, 40, 41.
Richards, T. W., 51, 283.
Richardson, O. W., 310.
Richmond, H. D., 203.
Rideal, E. K., 66, 67, 71.
Riding, R. W., 287.
Rienäcker, G., 206.
Riesenfeld, E. H., 69, 72, 283.
Rijn, P. J. van, 158.
Riley, H. L., 51.
Rinderspacher, M., 136.
Rippel, A., 216, 217.
Risch, C., 199.
Rising, M. M., 205.
Rivett, A. C. D., 33.
Robertson, G. J., 97.
Robertson, R., 318.
Robinson, C., 204.
Robinson, (Mrs.) G. M., 99.
Robinson, H., 290.
Robinson, P. L., 49, 50, 283.
Robinson, R., 99, 130, 134, 139, 155, 163, 171, 172, 173.
Robl, R., 190, 205.
Roche, 251.
Rode, O., 56.
Rodebush, W. H., 15.
Roell, E., 54.
Roger, R., 110, 111.
Rogers, C. W., 54.
Rogers, J. S., 293.
Rogers, R. A., 61.
Rojahn, C. A., 178.
Rolf, I. P., 231.
Roll, (Mme.) C., 150.
Rolla, L., 61.
Rona, P., 44, 241.
Rose, D. C., 292.
Rosenberg, J. E., 46.
Rosenblum, S., 292, 293.
Rosenbohm, 241.
Rosenhauer, E., 158, 159.
Rosenheim, A., 68, 105, 129.
Rosenheim, O., 252, 254, 255, 256.
Roth, F., 142.
Rothen, A., 66.
Rothmund, W., 28.
Ruark, A. E., 299.
Rubenstein, L., 152.
Rudberg, E., 36, 38.
Rüter, R., 208.
Ruff, O., 194.
Rule, H. G., 144.
Rupp, E., 183.
Russell, A. S., 190, 287, 293.
Russell, H. N., 299, 315.
Rutherford, (Sir) E., 284, 285, 288, 290.
Ruzicka, L., 112, 113, 115, 116, 118, 119.
Ryschkewitsch, E., 61.

Sabalitschka, T., 201, 225, 227.
Sack, E., 119.
Sackur, O., 14, 15, 16.

Sänger, R., 147.
Saha, M., 20.
Sahashi, Y., 162.
Salzmann, R., 92.
Sander, L., 154.
Sandstede, 167.
Sandved, K., 206.
Sapper, A., 105.
Sarkar, P. V., 72.
Saunders, F. A., 299.
Sawai, K., 166.
Sayce, L. A., 58.
Scatchard, G., 21, 24, 31, 33, 34.
Schäfer, W., 89.
Schames, L., 16.
Schamm, 251.
Schapiro, E., 93.
Scharrer, K., 196, 202.
Schauder, H., 184.
Scheibler, H., 98.
Schepp, R., 212.
Schidlof, A., 20.
Schiebold, 260.
Schiemann, G., 184.
Schiff, H., 120.
Schintz, H., 113, 115, 116.
Schleede, A., 286.
Schleicher, A., 206.
Schlesinger, N., 104.
Schliephake, O., 56.
Schlubach, H. H., 84.
Schmid, G., 34, 35, 36.
Schmid, L., 157.
Schmidt, A., 57, 158.
Schmidt, G. C., 282.
Schmidt, J., 120.
Schmidt, R., 128.
Schmidt, T., 70.
Schoeler, A., 172.
Schoeller, W. R., 195.
Schoenmaker, P., 69.
Schöpf, C., 183.
Schofield, R. K., 46.
Scholl, 155.
Schollenberger, C. J., 216.
Schoorl, N., 188, 191.
Schorning, A., 102.
Schottky, W., 19.
Schoú, S. A., 313.
Schreeberger, A., 191.
Schreiber, A., 95.
Schreiber, (Miss) N. E., 187, 191.
Schreiner, E., 21, 26, 36.
Schrenk, H. H., 192.
Schrenk, W. T., 195.
Schrödinger, E., 20.
Schroedter, E., 130, 138.
Schtschukarev, S., 282.
Schubert, F., 151.
Schulek, E., 189.
Schultz, 255.
Schultze, G., 95.
Schulze, G., 120.
Schumacher, 241.
Schumacher, E. E., 60.
Schwalbe, C. G., 212.
Schwartz, E., 207.
Schwarz, R., 63.
Schwegler, K., 179.
Scott, 251.
Šebor, J., 205.
Sedlatscheck, K., 183.
Seekles, L., 177.
Seibert, F. B., 204, 248.
Seka, R., 164.
Selkajov, N., 72.
Selle, H., 200.
Seltz, H., 33.
Senter, G., 111.
Serebrijski, 254.
Sewig, R., 309.
Sexauer, W., 63.
Shaw, F. R., 132.
Shaw, J. A., 189.
Shaw, P. E., 46.
Shedd, O. M., 216.
Shepherd, R. T., 66.
Sherman, 254.
Sherrill, M. S., 25.
Shinoda, J., 172.
Shive, J. W., 226.
Shrum, G. M., 320.
Sidgwick, N. V., 56, 127.
Siebert, E., 130.
Siegbahn, M., 206.
Siegert, H., 72.
Siegwart, J., 127.
Sieverts, A., 54.
Simms, H. S., 76, 81.
Simon, A., 70.
Simon, F., 13, 18, 19, 261.
Simon, R. H., 215.
Simonsen, J. L., 160, 161.
Simpson, T. P., 138.
Simson, C. von, 261.
Sjöberg, K., 92.
Sjollema, B., 177.
Skinner, A. F., 82.
Skinner, C. E., 213.
Skinner, D. G., 110.
Skinner, H. W. B., 288.
Slater, 240.
Slotta, K., 176.
Slotta, K. H., 185.
Smekal, A., 285.
Smeykal, K., 81, 82.
Smiles, S., 132.
Smith, A. H., 228.
Smith, G. B. L., 198.
Smith, G. F., 135.
Smith, H. C., 50, 283.
Smith, H. G., 310.
Smith, J. C., 134, 139, 173.
Smith, J. D. M., 109, 300.
Smith, W., 239.
Smits, A., 65, 69, 70, 287.

Smolik, L., 207.
Smyth, C. P., 144.
Snell, F. R., 33.
Sobotka, H., 202.
Soden, H. v., 130.
Someya, K., 190.
Sommerfeld, A., 266, 298.
Soper, F. G., 135.
Sourlis, A., 159.
Späth, E., 164, 165, 166, 167.
Spencker, K., 83.
Speyer, E., 158, 173.
Sponer, H., 311.
Sponsler, O. L., 228.
Spreckels, E., 130.
Springer, J., 212.
Stadler, F., 32.
Stadnikov, G., 176.
Stahl, 241.
Stahn, R., 62.
Stallings, J. H., 217.
Stammreich, H., 286.
Starck, G., 196.
Starkweather, H. W., 49.
Starling, 255, 256.
Staudinger, H., 127.
Staudt, W., 203.
Stegeman, G., 46.
Steiger, G., 196.
Stein, L., 157.
Steingroever, A., 93.
Stephenson, G. E., 49, 283.
Stephenson, R. E., 216.
Stern, H. T., 200.
Stern, O., 15, 19, 44.
Stetter, G., 281.
Stevens, T. S., 169.
Stewart, A. W., 305.
Stimson, F. J., 316.
Stintzing, H., 282.
Stock, A., 57, 59, 191.
Stoehr, C., 181.
Stoepel, P., 167.
Stoermer, R., 128.
Stoll, M., 113, 115, 116.
Stone, S. B., 50, 283.
Stoner, E. C., 300.
Stotz, E., 158, 159.
Strache, H., 211.
Strakosch, J., 120.
Straus, F., 98.
Strecker, W., 193, 194.
Stuart, N., 115.
Stubbings, W. V., 120, 125.
Stuhlmann, H., 178.
Stumpf, F., 287.
Sucharipa, R., 228.
Sugden, J. N., 27.
Sugden, S., 106, 131.
Suhrmann, R., 20.
Sur, N. K., 303.
Sur, R., 20.
Svanberg, O., 36.
Swart, E., 70.
Swindells, F. E., 26.
Széll, K., 20.
Szepessy, C., 225.
Szilard, L., 272.
Szymankiewicz, S., 56.

Tabern, D. L., 63.
Tadokoro, T., 228.
Täufel, K., 202.
Takahashi, B., 228.
Takane, K., 93.
Tammann, G., 35.
Tananaev, N. A., 186, 188.
Tarugi, N., 72.
Taylor, H. A., 27, 66.
Taylor, H. S., 30, 34.
Taylor, P. A., 261, 264, 266.
Taylor, T. W. J., 33, 127, 159.
Teeter, C. E., 31.
Tenney, F. G., 211.
Terni, A., 68.
Tetrode, H., 15, 16.
Thaysen, A. C., 212.
Thibaud, J., 288, 289, 290.
Thiede, B., 72.
Thiele, J. N., 306.
Thimann, M., 59.
Thomas, F., 194.
Thomas, J. S., 63.
Thomas, R. P., 214.
Thompson, A. P., 60.
Thoms, 100.
Thomson, (Sir) J. J., 43, 144, 147, 241, 246.
Thoræus, R., 206.
Thorne, P. C. L., 28.
Thorpe, J. F., 37, 161.
Tidmore, J. W., 219.
Tiede, E., 59, 286.
Tietze, E., 142, 143.
Tillmans, J., 203.
Timoféév, W. F., 31.
Titley, A. F., 149.
Tokarewa, A., 226.
Tolman, R. C., 12, 15, 16, 36.
Topping, J., 264.
Toussaint, L., 206.
Traube, W., 62.
Trautz, M., 31.
Travers, A., 192.
Treadwell, W. D., 197, 198.
Trkal, V., 16.
Tröger, J., 159.
Tropsch, H., 212.
Troquay, P. H., 206.
Truninger, E., 220.
Tschitschibabin, A. E., 157, 182.
Tschopp, E., 193.
Tschugaev, L., 73.
Tulin, A. F., 220.
Turley, H. G., 110, 111.

Turner, E. E., 104, 122, 123, 125, 137.
Turner, T. W., 217.
Tuwim, L., 294.
Twist, R. F., 132.
Twyman, 314, 316.

Uhlenbeck, G. E., 299.
Ullrich, E., 101.
Uloth, R., 20.
Unger, H., 158.
Ungerer, E., 220.
Urban, H., 230.
Urey, H. C., 16.
Urk, A. T. van, 52.
Urk, H. W. van, 190.

Valeton, J. J. P., 259.
Vanino, L., 190.
Vanni, A., 120.
Vegard, L., 320.
Velghe, M., 157.
Venator, W., 286.
Vesterberg, K. A., 60.
Vickery, H. B., 226, 227.
Vieweg, E., 102.
Visscher, 239.
Vivian, A. C., 55.
Vlastimil, 198.
Voegtlin, 241.
Vogel, R., 69.
Vollmer, 254.
Vorländer, D., 130, 133, 138.
Vortmann, G., 190, 191.
Voss, W., 98.
Votoček, E., 204.

Wachsztejński, J., 56.
Wada, I., 187, 195.
Waddell, 240.
Wagner, C., 32, 202.
Wahl, A., 153, 154.
Waksman, S. A., 211, 213.
Walach, B., 151.
Walbaum, H., 118.
Wales, H., 205.
Walker, N. H., 199.
Walker, O. J., 102.
Wallace, T., 221.
Wallach, O., 112.
Waller, I., 269, 271.
Warburg, 241.
Ward, A. M., 111.
Ward, T. J., 192.
Warnat, K., 171.
Warren, E. H., 102.
Warren, R. G., 197.
Warrington, A. W., 51.
Wartanian, W., 159.
Wasastjerna, J. A., 274.
Washburn, E. W., 282.
Watanabe, S., 228.
Webb, T. J., 12, 21, 29.
Webster, 254.
Wedekind, E., 103.
Weichselfelder, T., 72.
Weidemann, 251.
Weidling, H., 225.
Weigand, F., 89.
Weinland, R. F., 60, 105.
Weinstock, 254.
Weisbrod, F., 207.
Welling, W. F., 139.
Werner, A., 107, 291.
Werner, O., 225.
Wesolowski, W. A., 36.
Wessel, W., 46.
West, (Miss) H., 163.
West, J., 236, 240, 270, 276.
Westgarth, G. C., 75.
Westrip, G. M., 200.
Weston, F. R., 62.
White, J. W., 212.
Whitehead, 249.
Whitford, E. L., 203.
Whiting, A. L., 215.
Widdowson, W. P., 293.
Widmer, (Mlle.) R., 110, 150.
Więckovski, W., 64.
Wiederholt, W., 48.
Wieland, H., 141, 172, 183.
Wietzel, R., 13.
Wightman, W. A., 115.
Wijsenbeek, 237.
Wikul, M., 193.
Wilhelm, J. O., 273.
Wilhelmi, O., 154.
Wilkins, H., 106, 131.
Wilkinson, J. A., 63.
Wilkinson, J. F., 130.
Willers, C. U., 60.
Willey, E. J. B., 66.
Williams, E. J., 272.
Williams, J. G., 203.
Williams, J. W., 70.
Willimot, 252.
Wills, G. O., 110, 111.
Willstätter, R., 60, 63, 113, 232.
Wilson, B. D., 214.
Wilson, I. S., 130.
Wilson, J. K., 214.
Wind, 241.
Windaus, A., 162.
Winkler, L. W., 202.
Winter, 239, 240.
Wirtel, A. F., 202.
Wöhl, K., 18.
Wöhler, L., 56, 73.
Wokes, 252.
Wolf, A., 82.
Wolf, H., 196.
Wolff, L., 57, 177.
Wolfsohn, K., 92.
Wood, R. W., 302, 303.

Wood, T. B., 221.
Wood, W. A., 274.
Woodhouse, C. P., 159.
Wooster, W. A., 288, 290.
Wormall, 249.
Wrangell, M. von, 217.
Wrede, 256.
Wyckoff, R. W. G., 257, 264, 276.
Wylam, B., 90.

Yamada, N., 292.
Yntema, L. F., 61.
Young, G., 182.
Yovanovitch, D. K., 289, 290.

Zachariasen, W., 275.
Zawadzki, J., 56.
Zeidler, W., 19.
Zeise, 93.
Zelinski, N. D., 113, 176.
Zemplén, G., 88, 91.
Zetzsche, F., 192.
Ziegler, 255.
Zimmerli, A., 128.
Zimmermann, A., 120.
Zimmermann, P., 126.
Zintl, E., 206, 286.
Zobel, F., 180.
Zumstein, F., 123.
Zvegintzov, M., 33.
Zvjaginstsev, O., 72.
Zwick, K. G., 191.

INDEX OF SUBJECTS

Acenaphthpyridines, 161.
Acetaldehyde in plants, 225.
Acetic acid, density and freezing points of, 203.
  distribution of, between solutions, 27.
  basic beryllium salt, crystal structure of, 279.
  potassium salt, electrolysis of, 102.
  ethyl ester, solubilities of, in solutions, 27.
Acetic anhydride, determination of, 203.
Acetoacetic acid, α-hydroxy-, 98.
Acetone, *di*hydroxy-, determination of, 203.
Acetylacetone, metallic derivatives, crystal structure of, 278.
Acetylenes, detection of, 201.
Acetylenedicarboxylic acid, preparation of, 98.
Acetylindazoles, 179.
Acids, organic, 98.
  thallous salts, 99.
  weak, ionisation constants of, 25.
  analysis of, 208.
Activity coefficients, 22.
Activity coefficient product, 26.
Adzuki subtrilobata (adzuki bean), globulins from, 228.
Aetioporphyrin, synthesis of, 151.
*iso*Aetioporphyrin, 152.
d-Alanine, cobalt salts, 104.
Alcohols, detection of, 201.
Alkali halides, latent heat of sublimation of, 262.
  metals, detection and separation of, 187.
Alkaline earths, arc spectra of, 299.
Alkaloids, calumba root, 167.
  corydalis, 166.
  morphine, 172.
  *iso*quinoline, 163.
Alkyl halides, detection of, 201.
Alkylbarbituric acids, and their mercury derivatives, 183.
Allantoin, structure of, 184.
Alloys, spectrographic analysis of, 317.
Aluminium in acid soils, 221.
  hydroxide, forms of, 60.
  oxide, crystal structure of, 275.
  detection of, 187.
  separation of, from magnesium, 192.
"Aluminon," detection of rare metals with, 188.
Amines, primary aromatic, determination of, 204.
Amino-acids, determination of, 204.
Ammonium salts, configuration of, 102.
Amylobiose, 93.
Analysis, electrochemical, 206.
  gas, 200.
  inorganic, 186.
  organic, 201.
  physical, 205.
  spectroscopic, 314.
  water, 199.
Anhydrite, crystal structure of, 274.
4-Anilino-2-phenyl-6-methylpyrimidine, methylation of, 181.
Aniloquinolines, amino-, 159.
Antimony, determination of, 206.
Aporphine, synthesis of, 172.
Arginine, determination of, 203.
Arrhenatherum bulbosum, lævulosan from, 228.
Arsenic, determination of, 191.
  determination of, in organic compounds, 202.
Arsinosoquinone, chloro-, 162.
Asparagine in plants, 226.
Atoms, structure of, 282.
Atomic weights, 49.
Aurora, spectrum of, 318.
Azelaic acid, *di*hydroxy-, 101.
Azido*di*thiocarbonates, determination of, 198.
Azo-dyes, absorption spectra of, 205.

Bacillus prodigiosus in soils, 213.
Bacillus tuberculosis, hydrolysis of nucleic acid from, 182.
Bacteria in soils, 214, 215.
  resting, dehydrogenation by, 245.
Barbituric acid, benzoylation of, 182.
Barium aluminates, 57.
  oxide, reduction of, 57.
  vanadate, 68.
Bases, weak, analysis of, 208.
Beechwood, hemicelluloses of, 231.
Benzene, dipole moment of, 146.
  derivatives, physical properties of, 143.
  nucleus, substitution in, 129.
Benzenesulphonic acid, beryllium salt, 56.
Benzidines, *di*nitro-, 122.

Benzoic acid, 3 : 5-*di*nitro-, as reagent for alkaloids, 202.
Benzoylpyruvic acid, beryllium salt, resolution of, 103, 128.
Benzyl*iso*quinolines, 163.
Berberine, conversion of, into β-homochelidonine, 168.
Berberrubine, 167.
Beryl, crystal structure of, 270, 276.
Beryllium, preparation of, 55.
salts, properties of, 55.
oxide, crystal structure of, 275.
benzoylcamphor, 103, 128.
detection of, 188.
Biolase, 93.
αβ-Bisdihydro*iso*indylethane, 180.
Bismuth, separation of, 191.
Blood, glycolysis in, 240.
effect of insulin on sugar in, 238.
Boiling point of benzene derivatives, 143.
Boldine, 171.
Boron, atomic weight of, 49.
separation of isotopes of, 283.
hydrides, and their derivatives, 58.
sulphide, 59.
Brain, hydrolysis of cerebrosides of, 100.
Bromine, chemical constant of, 20.
detection of, 189.
Butterflies, pigments from wings of, 184.
tert.-Butylbenzene, nitration of, 141.

Cabbage, blue, extracts of, as indicator, 190.
Cadmium, vapour pressure of, 58.
Cæsium, line intensity in spectrum of, 301.
determination of, and its separation from rubidium, 193.
Calcite, density and shape of crystals of, 264.
Calcium alloys with mercury, 57.
fluoride, scattering power of, 271.
hydride, 53.
silicide, thermal analysis of, 56.
sulphate, effect of heat on, 56.
detection of, 187.
separation of magnesium from, 193.
Calumba root alkaloids, 167.
Camphor, and its derivatives, rotation of, 40, 41, 42.
Camphorquinone hydrazones, 128.
Carbohydrates, 74.
Carbon rings, large, 114.
*tetra*fluoride, 61.
*mon*oxide, combustion and oxidation of, 62.
determination of, 200.
*di*oxide, solid, crystal structure of, 273.
determination of, in water, 199.
Carbonyl groups, determination of, 203.
Carborundum, crystal structure of, 276.
Carboxyhæmoglobin, determination of, 318.
p-Carboxyphenylmethylethylarsine sulphide, enantiomorphous, 105, 129.
m-Carboxyphenyl methyl sulphoxide, resolution of, 107.
Castor oil, hydrogenation of, 100.
Catalysis, 35.
Cauliflower, proteins from, 228.
Cells, physiological, oxidation and reduction in, 243.
Cellobiose, structure of, 88.
Cello*iso*biose, 89.
Cellosan, 95.
Cellotriose, 89.
Celluloid, colloidal, preparation of, 198.
Cellulose, structure of, 95.
crystal structure of, 277.
decomposition of, in soils, 214.
cotton, acetolysis of, 96.
Cerium, preparation of, 60.
detection of, 188.
Chemical constants, 18.
Chlorine, atomic weight of, 50.
chemical constant of, 20.
*di*oxide, vapour pressure of, 71.
Hydrochloric acid, rotation spectrum of, 307.
distribution of, between benzene and salt solutions, 27.
Perchlorates, crystal structure of, 274.
determination of, 195.
detection and determination of, in water, 199.
determination of, in air, 200.
Chlorosis, effect of manganese on, 221.
Cholesterol, absorption spectrum of, 255.
antirachitic activation of, 253.
Chromium carbonyl, 70.
*tri*hydride, 72.
oxide, new, 70.
determination of, 192.
Chrysoberyl, crystal structure of, 275.
Chrysohermidin, 226.
"Citarin," use of, in analysis, 190.
Civetone, 119.
Cobalt salts, complex, 72.
hydride, 72.
detection of, 186, 187.
Codamine, 164.
Codeine, 172.
Columbium. *See* Niobium.
Complement, factors in, 249.
Compton effect, influence of, on scattering, 272.

Copper, deposition of, and its separation from bismuth, 206.
action of sulphuric acid on, 54.
sulphates, basic, 54.
detection of, 186.
determination of, 191.
Coptis japonica, alkaloid from, 167.
Coptisine, 167.
n- and *iso*-Corybulbines, 166.
Corydalis alkaloids, 166.
Cristobalite, crystal structure of, 276.
Cryptopine, synthesis of, 168.
Cryptopyrrole, synthesis of, 151.
Crystals, symmetry of, 258.
relation between chemical bonds and structure of, 266.
dynamics of lattice of, 260.
length of unit-cell edge of, 263.
reflexion of Röntgen rays by, 267.
rotation photographs of, 259.
scattering coefficient of, 269.
temperature factor for, 271.
diatomic, constants of, 266.
inorganic, 273.
organic, 277.
Cytochrome, 251.
Cytosine, reduction of, 182.

Debye's equation, 145.
trans-Decahydro*iso*quinoline, 162.
Dehydroquinine, arsenic compound of, 162.
Diabetes, effect of cobalt and nickel in, 238.
Diaminodi-iminodisilane, 63.
Diazines, 180.
Diazoles, 175.
Dicarbamidoethane, 184.
Dicentrine, 171.
cis- and *trans*-Dichlorodiammino-platinum, 73.
Dielectric constant of benzene derivatives, 144.
Diethoxymethylene, preparation of, 98.
Diguanide, determination of, 203.
Dihexosan, 92.
4 : 5-Dihydrouric acid, 5-amino-4-hydroxy-, 183.
Dihydroxytetraiodatostannic acid, 71.
$\alpha\delta$-Diketones, action of hydrazine on, 150.
β-Diketones, co-ordination compounds of, 103.
α- and β-Diketones, structure and properties of, 127.
Dimethoxyazelaic acid, 101.
Diphenic acids, resolution of, 123.
Diphenyl derivatives, 119, 137.
Diphenylamine as indicator, 190.
$\alpha\alpha$-Diphenyl-*n*-propyl alcohol, *l*-β-amino-, inversion of, 110.
Diphenylsilane, *di*chloro-, 63.
Diphenylthiocarbazone as reagent for metals, 186.
Di*iso*quinoline alkaloids, 165.
Disaccharides, 87.
Disalicylatoboric acid, resolution of, 105.
Dispersion, rotatory, 39.
Drying, intensive, effects of, 69.
Dyes, absorption of, by fibres, 109.

Earths, rare, prediction of spectra of, 300.
Ehrlich's test, colouring matters formed in, 151.
Electrification at surfaces, 43.
Electro-capillary curves, 47.
Electrochemical analysis, 206.
Electrodes, fluorine, potential of, 17.
gold-coated platinum, 207.
magnesium, for spectra, 205.
quinhydrone, 200, 207.
Electrolytes, solutions of, 21.
Element 61, 61.
Elements, disintegration and transmutation of, 284.
Elodea canadensis, polymerisation of formaldehyde by, 225.
Energy, free, determination of, 13.
Entropy, 11.
Enzymes, specificity of, 232, 233.
determination of, 233.
purification of, 233.
Equilibria, inner, effect of drying on, 69.
i-Erythritol, crystal structure of, 278.
Etch-figures, 258.
Ethylene*di*aminobisacetylacetone, cobalt co-ordination compound of, 109.
"Exaltone," 114.

Fats, action of hydrazine on, 101.
Ferro-silicon, chlorination of, 63.
Filters, light, 205.
Fluorine, oxidising reactions of, 71.
Fluoroaluminates, 60.
determination of, 196.
electrodes. *See under* Electrodes.
Formaldehyde, polymerisation of, 96.
in plants, 225.
detection of, 201.
determination of, 202.
Formic acid, action of ultra-violet light on, 98.
Fructose, structure of, 80.
di*iso*propylidene ether, 82.

Galactose, separation of, from other sugars, 204.
di*iso*propylidene ether, 82.

Garnet, crystal structure of, 276.
Gases, ionisation of, by α-particles, 291.
entropy of, 14.
Gas analysis, 200.
Gastric juice, detection of lactic acid in, 201.
Gems, crystal structure of, 275.
Gentiobiose, synthesis of, 89.
Germanium, atomic weight of, 50.
detection of, 188.
Germanochloroform, 63.
Glaucine, 171.
Glucal in diabetes, 240.
Glucosan in diabetes, 240.
Glucose, mutarotation of, 38, 86.
di*iso*propylidene ether, 82.
Glucose, 3-chloro-, 84.
Glucoseureide, 85.
Glutathione, synthesis of, 176.
Glycerol, entropy of, 13.
Glycolysis, 240.
Glyoxalines, 175.
Glyoxaline-4′(or 5′)-carboxy-*p*-aminophenylarsinic acid, 175.
Glyoxylic acid, preparation of, 98.
Gold, conversion of mercury into, 285.
determination of, 207.
Graminin, 228.
Graphite, melting point of, 61.
Groups, orienting influence of, 137.

Hæmochromogens, 250.
Hæmoglobin, 249.
osmotic pressure and molecular weight of, 251.
Hafnium, detection of, 188.
separation of zirconium from, 64.
Halides, determination and separation of, 207.
Halogens, determination of, in mixtures, 196.
Halogen hydrides, chemical constants of, 20.
Helium, atomic weight of, 49.
preparation of, from hydrogen, 51.
continuous emission spectrum of, 304.
liquid, surface tension of, 52.
Heptamethoxytriphenylcarbinol as indicator for hydrogen ions, 199.
Hermidin, and cyano-, 226.
Hexacosoic acid from arachis oil, 100.
Hexamminogermanic chloride, 63.
n-Hexane, effect of drying on, 70.
s-Homotetrahydro*iso*quinoline, 162.
Humic acid in soils, 210.
Hydantoins, 176.
Hydrazones, configuration of, 127.
Hydrides, spectra of, 311.
Hydrocarbons, polymorphism of, 278.
Hydrocellulose, molecular weight of, 97.
Hydrochloric acid. *See under* Chlorine.
Hydrogen, effect of drying on combination of halogens and, 71.
*per*oxide, reaction of iodine with, 31.
Hydrogen ions, determination of, in water, 199.
Hydroxylamine, detection of, 189.
determination of, 198.
Hydroxypentamminoplatinic carbonate, 73.
Hypnotics, alkylbarbituric acids as, 183.
Hypoglycæmia, insulin, 239.

Illinium, 61.
bis-Imino-acids, copper salts, 104.
Indazoles, 178.
Indazyl-fatty acids, 178.
Indigotin, formula of, 154.
Indium, separation of, from its alloys, 195.
Indole derivatives, 152.
Inulin, acetylation of, 97.
Insulin, 238.
Invertase, yeast, isolation of, 232.
Iodine, chemical constant of, 20.
effect of drying on combination of hydrogen and, 71.
reaction of hydrogen peroxide with, 31.
Iodates, detection of, 189.
Ions, entropy of, in solutions, 17.
hydration of, in aqueous solutions, 27.
gaseous, energy changes in solution of, 29.
positive, emission of, from heated salts, 282.
Ionisation constants, 25.
Ionium, life-period of, 294.
Iron hydrides, 72.
oxide, scattering power of, 271.
Steel, spectrographic analysis of, 318.
determination of, 192, 206.
Isatan, true nature of, 153.
Isatide, true nature of, 154.
Isatin, action of ammonia on, 153.
derivatives, 153.
Isotopes, 280.
spectra of, 284.
separation of, 282.

Kaufler formula, 108, 120.
κ-Ketobehenic acid, 99.
δ-Ketomyristic acid, 99.

Ketones, racemisation of, 111.
cyclic, 112.
κ-Ketononadecoic acid, 99.
ι-Ketostearic acid, 99.

Lactic acid in muscle, 242.
d-Lactic acid, ethyl ester, inversion of, 110.
Lactones, acid, catalysis of formation of, 34.
Lactose, structure of, 89.
Lactic acid, detection of, 201.
Lamp, quartz lead, 65.
Lanthanum, preparation of, 60.
ψ-Laudaline, 164.
Laudanine, 164, 165.
Laudanosine, 165.
Lead, atomic weight of, 51.
β-ray spectrum of, 289.
spectra of isotopes of, 284.
transmutation of, 65.
separation of silver from, 191.
Leaves, cell sap of, 227.
Leucopterin, 183.
Lichosan, 96.
Lignin from wood, 230.
relation of humic acid to, 210.
Lignocellulose, 230.
Linen, Egyptian, humic matter of, 212.
Liquids, entropy of, 11.
Lithium, isotopes of, 282.
Lucerne, nitrogenous constituents of, 227.

Magnesium silicide, thermal analysis of, 56.
separation of calcium and, 193.
Maltose, structure of, 87.
*iso*Maltose, synthesis of, 89.
Manganese, effect of, on chlorosis, 221.
Permanganates, crystal structure of, 274.
determination of, 192.
Melezitose, 91.
Melting point of benzene derivatives, 143.
Mercuration of aromatic compounds, 141.
Mercurialis, hermidin from, 226.
Mercury, isotopes of, 280.
spectra of isotopes of, 284.
vapour pressure of, 58.
surface phenomena of, 46.
conversion of, into gold, 285.
vapour, absorption spectrum of, 302.
toxicity of, 57.
alloys with calcium, 57.
Mercurous halides, parameters of, 270.
Mercury, detection of, 205.
determination of, 191.
determination of, in organic compounds, 202.
Melanism in moths, 248.
Mesothorium-2, purification and spectra of, 289.
half-period of, 293.
Metals, stopping power of, for α-particles, 292.
detection of, 186.
Metallic salts, reduction of solutions of, 53.
hydrides, 53.
Methæmoglobin, oxygen content of, 251.
Methanesulphonic acid, chlorobromo-, resolution of, 108.
Methyl alcohol, determination of water in, 205.
5-Methylcytosine from *Bacillus tuberculosis*, 182.
4-Methyldiphenyl sulphoxide, 4′-amino-, resolution of, 107.
2 : 3 - Methylenedioxy - 11 : 12 - dimethoxy - 6 : 15 : 16 : 17 - tetrahydroparaberine, 170.
3 : 4 - Methylenedioxyhomophthalic acid, preparation of, 169.
2 : 3-Methylenedioxyoxyprotoberberines, 166.
Methylenepapaverine, 164.
α-, β-, and γ-Methylglucosides, 74, 75.
5-Methylindazole, 7-amino-, acetyl derivatives, 180.
Methylmorphimethines, 173.
dl-1-Methyl-1 : 2 : 3 : 4-tetrahydro-β-naphthaquinoline, 160.
Molecular asymmetry and rotation, 43.
structure in relation to band spectra, 310.
Molybdenum, determination of, 195.
Monosaccharides, 83.
Morphine, detection of, 202.
Morphine alkaloids, 172.
Moths, melanism in, 247.
Muscle, lactic acid in, 242.
Muscone, 118.
Musk, substitute for, 114.
Mutarotation, 37, 85.
Myristic acid, esters, 102.

Naphthalene, absorption spectrum of, 313.
Naphthaquinolines, 160.
Naphtha*iso*quinolines, 163.
β-Naphthylamine, action of paraldehyde with, 160.
Narcotine *N*-oxide, 163.
Neodymium, preparation of, 60.
Neolactose, 90.

Neopine, 173.
Nervonic acid, 100.
Nickel oxide, 53.
  detection of, 187.
  determination of, in fats, 318.
Niobium, detection and determination of, 194.
Nitella, absorption of halogens by, 223.
Niton. *See* Radon.
Nitrification in soils, 214.
Nitro-compounds, determination of, 204, 207.
Nitrogen, active, heat of formation of, 65.
  supply of, to plants, 216.
  *mon*oxide (*nitrous oxide*), synthesis of, 66.
    solid, crystal structure of, 273.
  *tet*roxide, effect of drying on, 69.
    spectroscopic determination of, 318.
  *pent*oxide, thermal decomposition of, 66.
  Nitrates, detection of, 189.
    determination of, 202.
Nitroso-compounds, determination of, 207.
*cyclo*Nonanone, 113.

Δ^{λ}-Octadecinenoic acid, 100.
*cyclo*Octanone, 113.
Œstrin, 237.
Olivine, crystal structure of, 275.
Optical activity, 39, 102.
  inversion, Walden's, 110.
  superposition, 41.
Orientation in aromatic substitution, 129.
Oryzanin from rice, 228.
  hydrolysis of, 162.
Ovary, hormone from, 237.
Oxaluric acid, 184.
Oxidation, biological, 243.
Oximes, configuration of, 127.
Oxygen, auroral green line in spectrum of, 320.
  dissolved, determination of, in water, 199.
Ozone, determination of, in air, 205.

Palmatrubine, 167.
Palmitic acid, esters, 102.
ψ-Papaverine, 164.
Paraberine, 170.
Particles, long-range, 292.
α-Particles, ionisation of gases by, 291.
  scattering of, 284.
  stopping power of metals for, 292.
  capture and loss of electrons by, 292.
Pasture grass, mineral content of, 221.
Peas, Norwegian, phosphatides of, 231.
Peat, ageing of, 208.
Pectic acid, 228.
Pectic substances, 228.
Pectin, 228.
Pentamethyl glucose, 85.
Perchlorates. *See under* Chlorine.
Permanganates. *See under* Manganese.
Phaseolus, allantoic acid in, 227.
Phenanthra*iso*quinolines, 171.
Phenols, nuclear alkylation of, 142.
  detection of, colorimetrically, 202.
Phenols, *di*hydroxy-, distinction between, 202.
l-Phenylalanine, 3 : 4-*di*hydroxy-, from tyrosine, 247.
4-Phenyl-4′-carbethoxybispiperidinium-1 : 1′-spiran bromide, resolution of, 102.
Phenyl-α-naphthylbenzylmethylarsonium iodide, optically active, 105.
Phosphatides of plants, 231.
Phosphorus, modifications of, 67.
  nitride and *sub*oxide, 68.
  Phosphates in soils, 217.
    determination of, 207.
Piperazines, 180.
Piperazinebisdihydro*iso*indolinium bromide, 180.
Plants, permeability of, for salts, 223.
  nutrition of, 216.
  carbon compounds in, 225.
  nitrogenous metabolism of, 226.
  phosphatides of, 231.
  frost resistance of, 231.
  leguminous, calcium supply to, 226.
Plant fibres, *X*-ray analysis of, 228.
Plant tissues, constituents of, 228.
Plaster of Paris, setting of, 56.
Platinum *tri*bromide and iodides, 72.
  separation of, 194.
Platinum metals, determination of, 206.
  separation of, 189.
Pneumococcus, specific substances from, 248.
Polonium, α-particles from, 291.
Polymethylenedicarboxylic acids, 101.
Porphin, 152.
Porphyrins, metallic compounds of, 250.
Potassium, radioactivity of, and its effect in geology, 291.
  ammoniostannite, 67.
  *tri*nitride, crystal structure of, 273.
  determination of, 193.
Potential, differences of, at surfaces, 44.

Praseodymium, preparation of, 60.
black oxide of, 61.
Propane, *αβγ -tri*amino-, co-ordination compounds of, 109.
Propiolic acid, and its anhydride, preparation of, 98.
*iso*Propylidenedioxy-groups, determination of, 203.
Proteins, tryptophan content of, 203.
vegetable, isoelectric points of, 227.
Protopectin, 228.
Protopine, synthesis of, 168.
Prussian blue, 72.
Purines, 183.
Pyrazine derivatives, 180.
Pyrazoles, 176.
Pyridine, preparation of, 156.
degradation of, 156.
hydrazinedisulphonate, 67.
Pyridines, 157.
Pyridinium *per*chlorate in acidimetry, 189.
2-Pyridone derivatives, 157.
Pyrimidines, 181.
Pyrosulphuryl chloride. *See under* Sulphur.
Pyrrole derivatives, 150.
Pyrryl ketones, 151.

Quartz, crystal structure of, 276.
Quinine as indicator, 190.
detection of, 201.
Quinol, determination of, 204.
Quinolines, 158.
*iso*Quinoline alkaloids, 163.
derivatives, 162.

Racemoids, recognition of, 108.
Radioactive constants, 293.
nuclei, structure of, 287.
Radioactivity, measurement of, 294.
heat developed in, 290.
Radium, β-ray spectrum of, 287.
β-ray spectra of disintegration products of, 289.
Radium-*B* and -*C*, half-periods of, 293.
Radium-*E*, decay constant of, 293.
Radon, α-particles from, 292.
decay constant of, 293.
" Raies ultimes," 314.
Rays, cosmic, 294.
Röntgen, reflexion of, by crystals, 267.
α-Rays, 291.
β- and γ-Rays, emission of, 287.
γ-Rays, heating effect of, 290.
Reactions, specific, 248.
Rhamnose, structure of, 78.
Rhodium chlorides and oxides, 73.
separation of, from platinum, 195.
Rice, proteins from, 228.
Rock-salt, scattering power of, 269.
Rotation photographs, 259.
Rubber, crystal structure of, 277.
Rubidium, line intensity in spectrum of, 301.
radioactivity of, 294.
bromide, scattering power of, 272.
determination of, and its separation from cæsium, 193.
Ruthenium *tetra*chloride, 73.
detection of, 188.
Ruthenonitrosopyridinodioxalic acid, potassium salt, resolution of, 104.

Samarium, preparation of, 60.
Sarcosine glucoside, 84.
Scattering coefficient of crystals, 269.
Secretin, 237.
Secretions, internal, 234.
Selenic-uranic acids, 70.
Selenium, determination of, in organic compounds, 202.
Serum, complement of, 249.
Shark, Greenland, oil from liver of, 252.
Silicon, atomic weight of, 49.
*di*oxide (*silica*), entropy of, 13.
Silver, atomic weight of, 50.
*per*chlorate, solubility of, in toluene, 55.
detection of, 186.
separation of lead from, 191.
Sinomenine, 171.
Slag, basic, determination of fluorine in, 197.
Sodium vapour, continuous absorption spectrum of, 303.
ammoniostannite, 67.
*tri*nitride, crystal structure of, 273.
thiosulphate, standard solutions of, 189.
detection of, in presence of potassium and magnesium, 177.
determination of, 193.
Soils, algæ in, 213.
bacteria in, 214, 215.
bases in, 220.
humus in, 209.
liming of, 212, 220.
nitrification in, 214.
phosphates in, 217.
effect of sulphur on, 215.
acid, aluminium in, 221.
Solids, entropy of, 11.
Solid state, complexity of, 69.
Solutions, velocity of reaction in, 30.
of electrolytes, 21.
aqueous, potential differences at surface of, 45.

Soy-beans, lecithin from, 231.
Spectra, intensity of lines in, 301.
of isotopes, 284.
absorption atomic, 302.
band, 305.
electronic changes and, 308.
line, 296.
mass, 280.
molecular, 304.
β-ray, 288.
Röntgen ray, 300.
rotation, 307.
series, multiplets in, 299.
Spectrograph, *X*-ray, 205.
Spectrometer, *X*-ray, 205.
Spectroscope, reversal, 318.
Spectroscopic analysis, 314.
Spermidine, 256.
Spermine, 255.
Stanni-iodic acid. *See under* Tin.
Starch, structure of, 92.
methylation of, 94.
iodide, iodine content of, 205.
Stearic acid, esters, 102.
Stearic acid, λ-hydroxy-, ethyl ester, 100.
Stearic acids, hydroxy-, 99.
Stearolic acid, reduction of, 99.
Stearolactone, crystalline, 100.
Steel. *See under* Iron.
Stereochemistry, 119.
Strontium, detection of, 187.
Strychnos nux vomica, alkaloid content of, 227.
Styrylquinolines, amino-, 159.
Suberic acid, $\alpha\alpha'$-dibromo- and $\alpha\alpha'$-*di*hydroxy-, 101.
Substitution in aromatic compounds, 129.
Sucrose, structure of, 90.
inversion of, 33.
Sugars, structure of, 74.
mutarotation of, 37, 85.
oxidation of, 84.
nitrates of, 85.
Sulphoxides, constitution of, 107.
resolution of, 126.
Sulphur, isotopes of, 281.
valencies of, 107.
*trio*xide, drying of, 69.
Pyrosulphuryl chloride, preparation and properties of, 70.
Sulphates, crystal structure of, 274.
determination of, 198.
Sunlight, effect of, on radioactivity, 294.
Surfaces, electrification at, 43.
Surface tension of charged surfaces, 47.
Sylvine, etch-figures of, 258.

Tellurium, determination of, 195, 206.
Tetrahexosan, 92.
Tetrahydrocolumbamine, 167.
Tetramethyl γ-fructose, 81.
Tetramethyl glucose, mutarotation of, 85.
Tetramethyl γ-glucose, 76.
Thallium silicates, 60.
determination of, 193.
Thebaine, 172.
Thermodynamics, third law of, 11.
Thorium, β-ray spectra of disintegration products of, 289.
Thorium-*C*, α-rays from, 293.
Thoron, half-period of, 293.
Thyroxine, 234.
Tin :—
Stannous phosphates, 63.
Stanni-iodic acid, 71.
Tissues, washed, 245.
Titanium, atomic weight of, 51.
detection of, 188.
p-Toluenesulphinic acid, ethyl ester, constitution of, 106.
p-Toluenesulphonic acid, beryllium salt, 56.
Transmutation, 284.
3 : 4 : 6-Triacetyl-2-*tri*chloroacetylglucose, β-chloro-, 83.
Tridymite, crystal structure of, 276.
Tricitin, 228.
Trihexosan, 92.
Trihydroxytri-iodatoantimonic acid, 71.
Tri-iminodisilane, 63.
Tripyrocatechylarsenic acid, resolution of, 105, 129.
Triticum repens, lævulosan from, 228.
Tritopine, 164.
Truxillic acids, 128.
Tuberculin, active principle of, 248.
Tumour tissues, glycolysis in, 241.
Turacin, 251.
Turanose, 91.
Tyrosine, action of tyrosinase on, 247.

Umbelliferone as indicator, 190.
Uranium nitrides, 71.
Uranous sulphate in determination of ferric salts, 190.
detection of, 188.
determination of, 194.
Uric acid, oxidation of, 184.
Uric acid glycols, degradation of, 184.

Valonia, absorption by cells of, 224.
Vanadium :—
Vanadous sulphate, reducing action of, 190.
Vanadates, 69.
detection of, 188.
determination of, 195.

Velocity of reaction in solutions, 30.
Vitamin-*A*, 251, 252.
Vitamin-*B*, 252.
Vitamin-*D*, 253.
Vitasterol, 255.

Walden inversion, 110.
Water, ionisation of, in solutions, 25.
analysis, 199.
Waxes, synthetic, 101.
Wheat, nutrition of, 224.
winter, 231.

Xanthopterin, 183.
Xanthopyrrolecarboxylic acid, synthesis of, 151.
Xylose di*iso*propylidene ether, 83.

Yatrenum as indicator, 190.
Yeast, nitrogenous constituents of, 227.

Zinc, vapour pressure of, 58.
in animal organisms, 314.
detection of, 186.
Zirconium, preparation of, 64.
detection of, 188.
separation of, 194.
separation of hafnium from, 64.

QL
1
C57
v.23
1926

UNIV OF MAINE
3 7550 00874936 9